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DEVELOPMENT OF THE FASTER PROCESS FOR REMOVING KRYPTON-85, CARBON-14, AND OTHER CONTAMINANTS FROM THE OFF-GAS OF FUEL REPROCESSING PLANTS*

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Abstract

The Oak Ridge Gaseous Diffusion Plant has the primary responsibility for the development of the FASTER (Fluorocarbon Absorption System for Treating Effluents from Reprocessors) process for application to LMFBR and LWR fuel reprocessing plants. Krypton-85 removals in excess of 99.9% and carbon-14 as carbon dioxide removals greater than 99.99% have been obtained in a development pilot plant. So far, pilot plant tests show that the presence of other reprocessing plant off-gas components does not appreciably affect the general operability or removal efficiency of the process. Tests also indicate that the one process designed for krypton and carbon removal may be even more effective in removing other fission products and objectionable chemical contaminants such as nitrogen dioxide. Elemental and organic iodine removals in excess of 99.99% and nitrogen dioxide removals over 99% were recently achieved. Higher process decontaminations are possible. Trapping studies show that 13X molecular sieves are very effective in removing the fluorocarbon vapor from the process product stream.

I. Introduction

Stringent emission standards are being formulated to limit the release of various volatile fission products from nuclear fuel cycle facilities. At this time, the viability of the nuclear fuel cycle rests, in part, on how well the industry can effectively manage all the associated nuclear wastes. The long-lived isotopes of krypton and carbon are of particular concern because the control technology has not yet been adequately demonstrated for removing either of these two fission products from the off-gas of commercial nuclear fuel reprocessing plants. The generally straightforward problem of off-gas decontamination is greatly complicated in this case by the presence of other common reprocessing plant off-gas components such as nitrogen oxides (NO , N_2O , NO_2), carbon dioxide, water, iodine, various organics, ruthenium tetroxide, and particulates. In the case of carbon-14, it is generally assumed that the volatile form of carbon will be carbon dioxide, although admittedly, quantities of carbon monoxide and light organics such as methane could also be present.

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Oak Ridge has the primary responsibility for the development of the FASTER (Fluorocarbon Absorption System for Treating Effluents from Reprocessors) process for removing krypton-85, carbon-14, nitrogen oxides, and possibly other contaminants from the off-gas of LMFBR and LWR fuel reprocessing plants. This work is being supported by the Division of Nuclear Fuel Cycle and Production of the United States Energy Research and Development Administration. The overall program is divided into four major areas: (1) process development, (2) process application, (3) solvent chemistry, and (4) reliability analysis. Process development is being done at the Oak Ridge Gaseous Diffusion Plant (ORGDP) in an existing pilot facility built specifically to study application of the FASTER process to reprocessing plants. Process application studies are being performed at both ORGDP and the Oak Ridge National Laboratory (ORNL), while the solvent chemistry work is being performed solely at ORNL. Kaman Sciences Corporation, Colorado Springs, Colorado, has been given a contract to perform the process reliability analysis. The main objective of the process development work is to generate all process technology required to completely define the fluorocarbon-based process for the reprocessing plant application. Process application studies will provide design models required for process optimization and conceptual plant design. This work will identify relative effects and importance of individual process elements and operating conditions on the overall system function. The solvent chemistry effort will establish and/or confirm component solubilities, phase relationships, component interactions, and corrosion characteristics of the fluorocarbon system. The process reliability studies proposed by Kaman will evaluate the FASTER process reliability and recommend necessary flow sheet redundancy and backup support systems to ensure a high process on-line efficiency. The overall program effort will culminate in the detailed design and economic evaluation of an off-gas decontamination facility applicable to commercial LMFBR and LWR reprocessing plants. ORGDP and ORNL share the responsibility for the LMFBR design, while the Savannah River Laboratory (SRL) has the responsibility for the LWR application.

Recent pilot plant data are presented and discussed in this report, along with the initial results obtained from the solvent chemistry program. The reliability analysis will be available later as an ORNL report. Process application work has only recently begun, and progress in this area will also be available later.

II. Pilot Plant Description

Figure 1 is a schematic of the ORGDP selective absorption pilot plant. Figure 2 is a photograph of the facility. Four packed columns comprise the main working sections of the process. The first three columns are designed to exploit certain gas-liquid solubility differences that exist between the solvent and the various volatile feed gas constituents. The solvent still, on the other hand, is designed to take advantage of vapor pressure differences between the solvent and the high boiling feed gas components. The main separation of contaminants is accomplished in the absorber. The other columns function in a variety of ways to separate and isolate the feed gas components dissolved in the solvent during the absorption step and ultimately purify the solvent for recycle. Other process equipment includes a process gas compressor, solvent pump, gas and solvent heat

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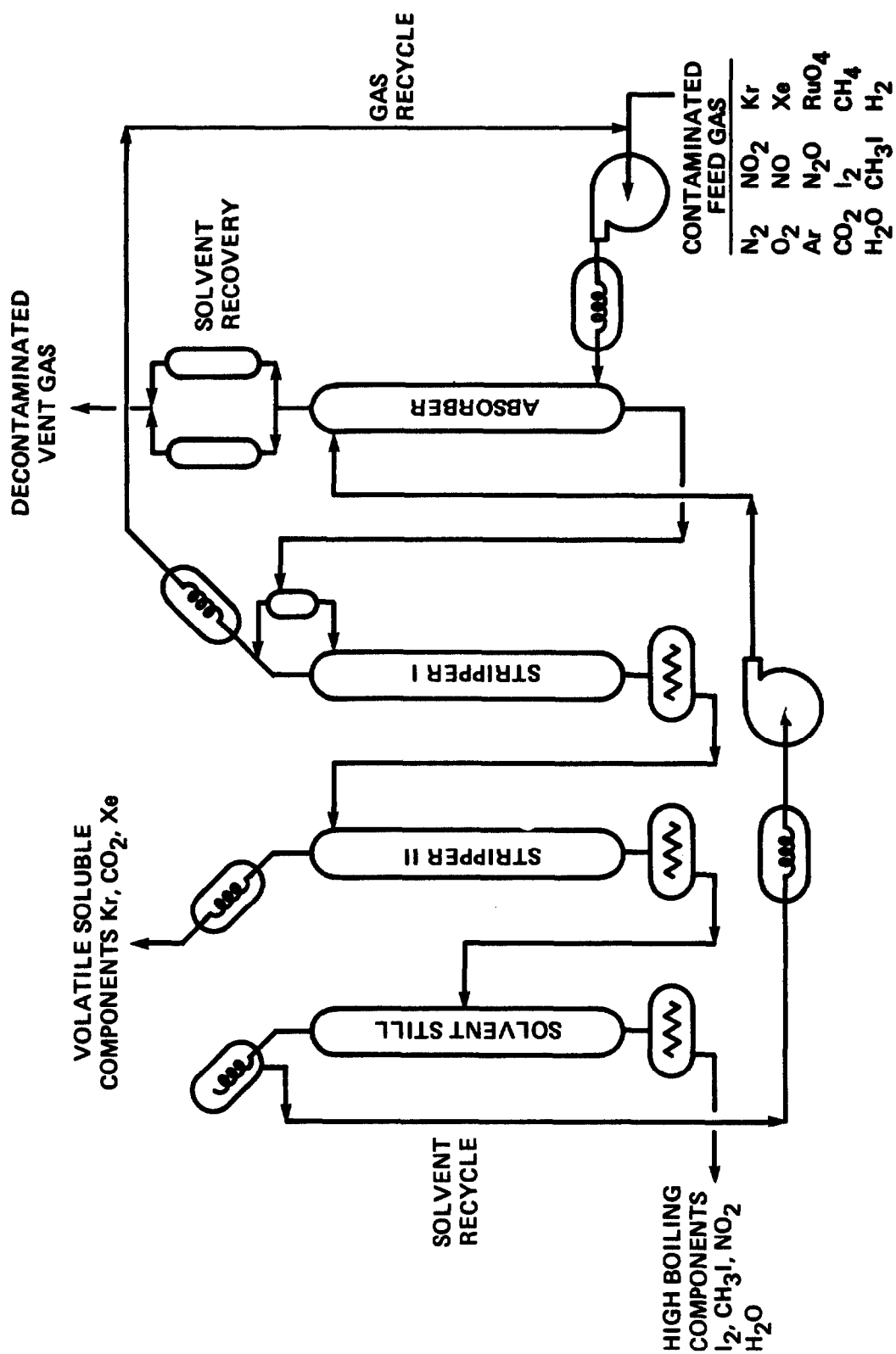


Figure 1. Schematic of the JRGDP Selective Absorption Pilot Plant

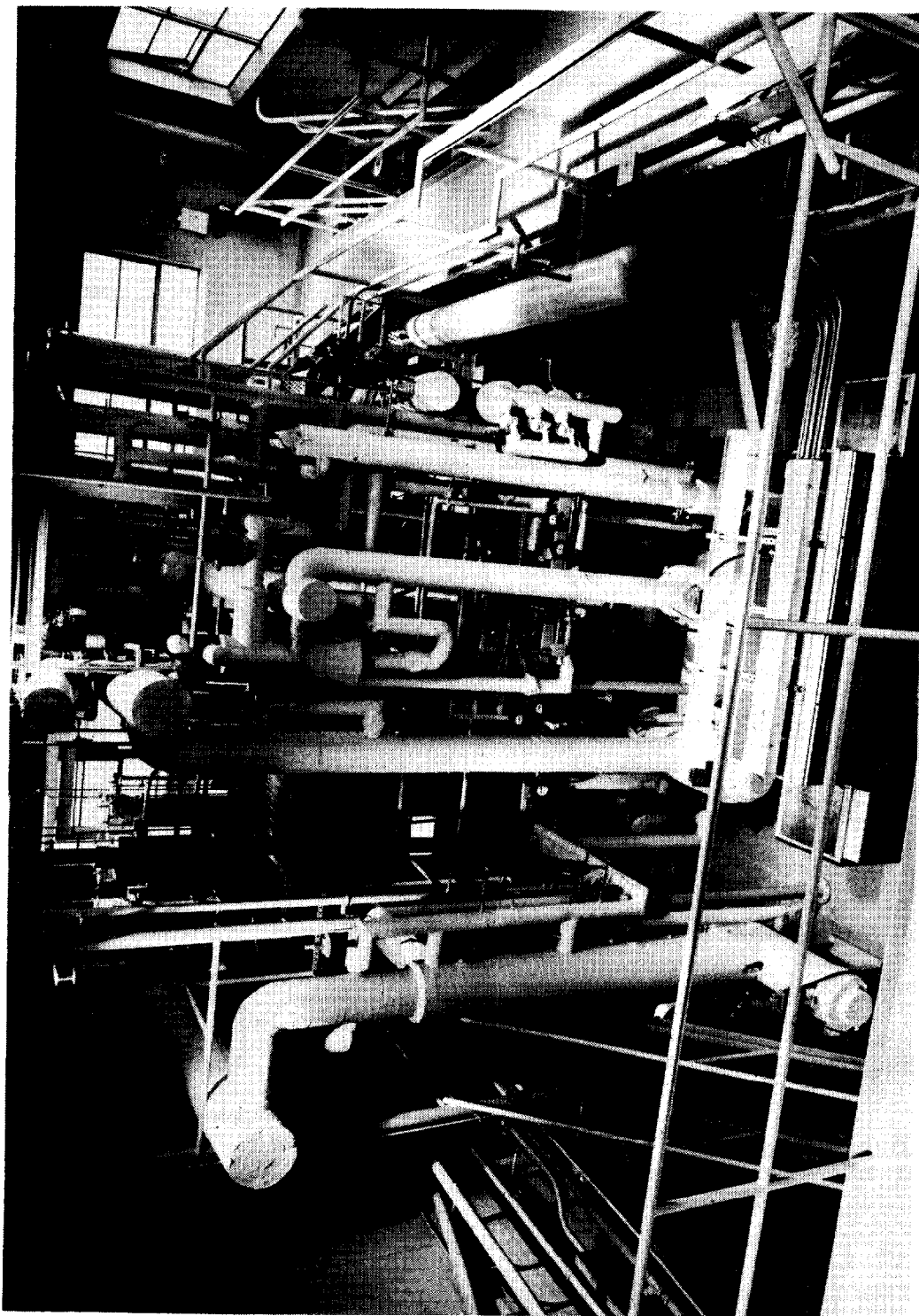


Figure 2. Overall View of the ORGDP Selective Absorption Pilot Plant

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exchangers, and several refrigeration compressors. Physical and chemical traps are also installed for solvent recovery and final product separation and purification. Details of the process and development pilot plant are available in several program reports [3,4,5].

III. Experimental Program Plan

As currently envisioned, the krypton-85/carbon-14 removal process will be the final step in an integrated chain of processes designed to collectively decontaminate fuel reprocessing plant off-gas. The integrity and reliability of any off-gas decontamination system will undoubtedly be the subject of much scrutiny. Legitimate concern will be expressed not so much about how well the off-gas train will function in a normal operation, but about the overall consequences of abnormal operation and the capability of the individual processes to meet the challenges imposed by irregular or otherwise uncontrolled feed conditions. In this context, several fundamental questions need to be answered: (1) what happens in the event the upstream primary removal equipment fails and large amounts of other fission products and chemical contaminants inadvertently pass downstream; (2) can the downstream process(es) be relied upon as a short-term backup system to remove the other radioactive components from the reprocessing plant off-gas in case of such a failure; and (3) how well can the fluorocarbon process function as the primary removal facility for iodine and other fission products, including ruthenium oxides, and chemical contaminants such as nitrogen dioxide. Pilot plant work is currently being directed toward exploring these points by establishing the general process behavior of feed gas components such as nitrogen oxides, iodine, methyl iodide, and water, and defining the effects of these components on the general operability and overall performance of a process designed for krypton-85 and carbon-14 removal.

Figure 3 gives the relative solubilities of various volatile feed gas components in the process solvent, refrigerant-12. Xenon and carbon dioxide are the most soluble of this group, while helium is the least. Figure 4 gives the predicted distribution coefficients of important feed gas components that are classified as high boiling components relative to the solvent. Those components more volatile than refrigerant-12 end up in either the process vent with the less soluble components, such as nitrogen and oxygen, or in the process product stream with the more soluble volatile components, such as krypton and carbon dioxide; while the less volatile components, i.e., iodine and nitrogen dioxide, collect in the solvent still reboiler. Water, not shown in figure 4, is more volatile than iodine but significantly less volatile than methyl iodide. Because krypton and xenon removals in excess of 10^3 were achieved previously, high process removals were projected for the even less volatile feed gas components.

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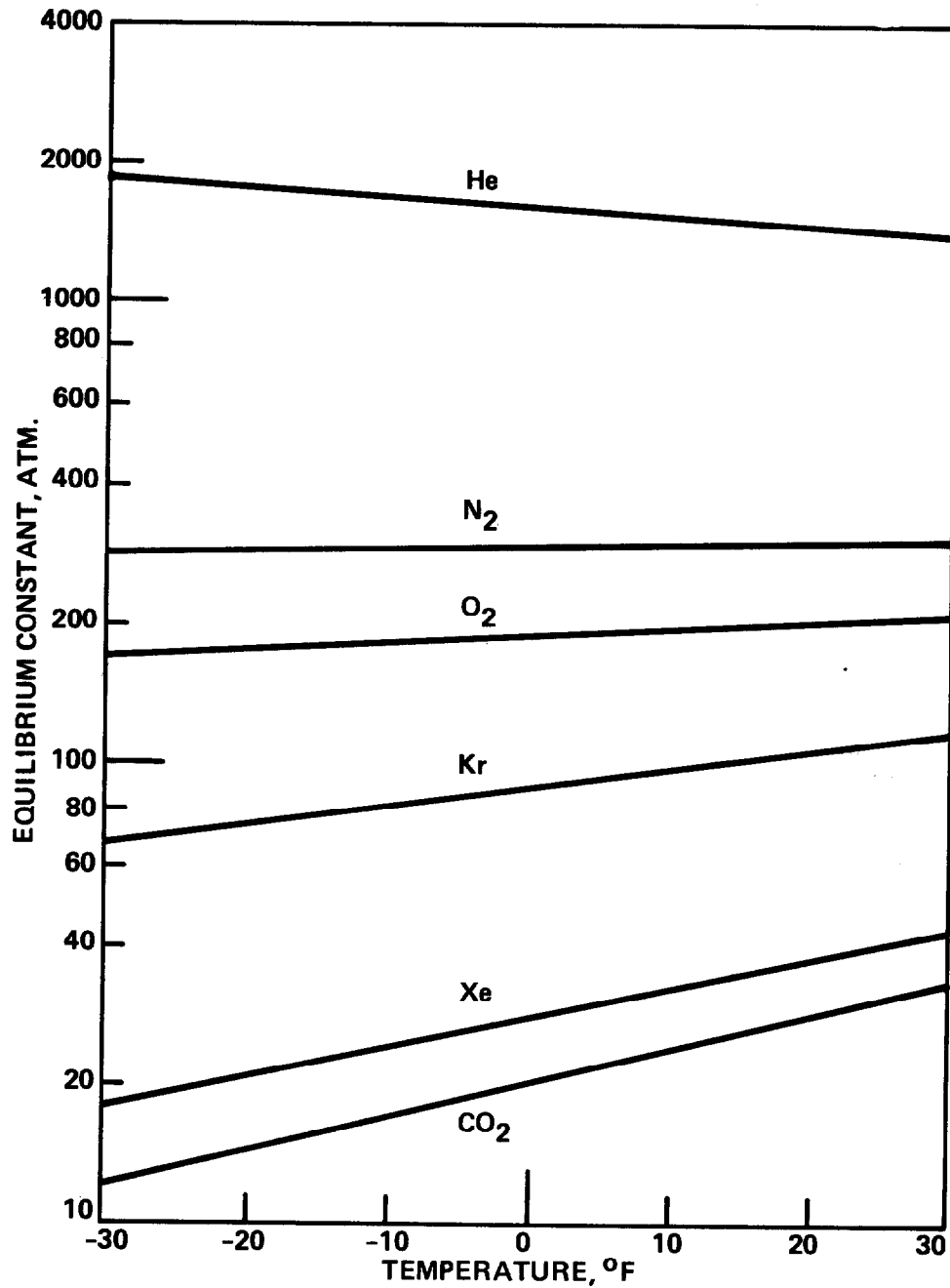


Figure 3. Equilibrium Distribution Coefficients of Various Feed Gas Components in Refrigerant-12 (CCl_2F_2).

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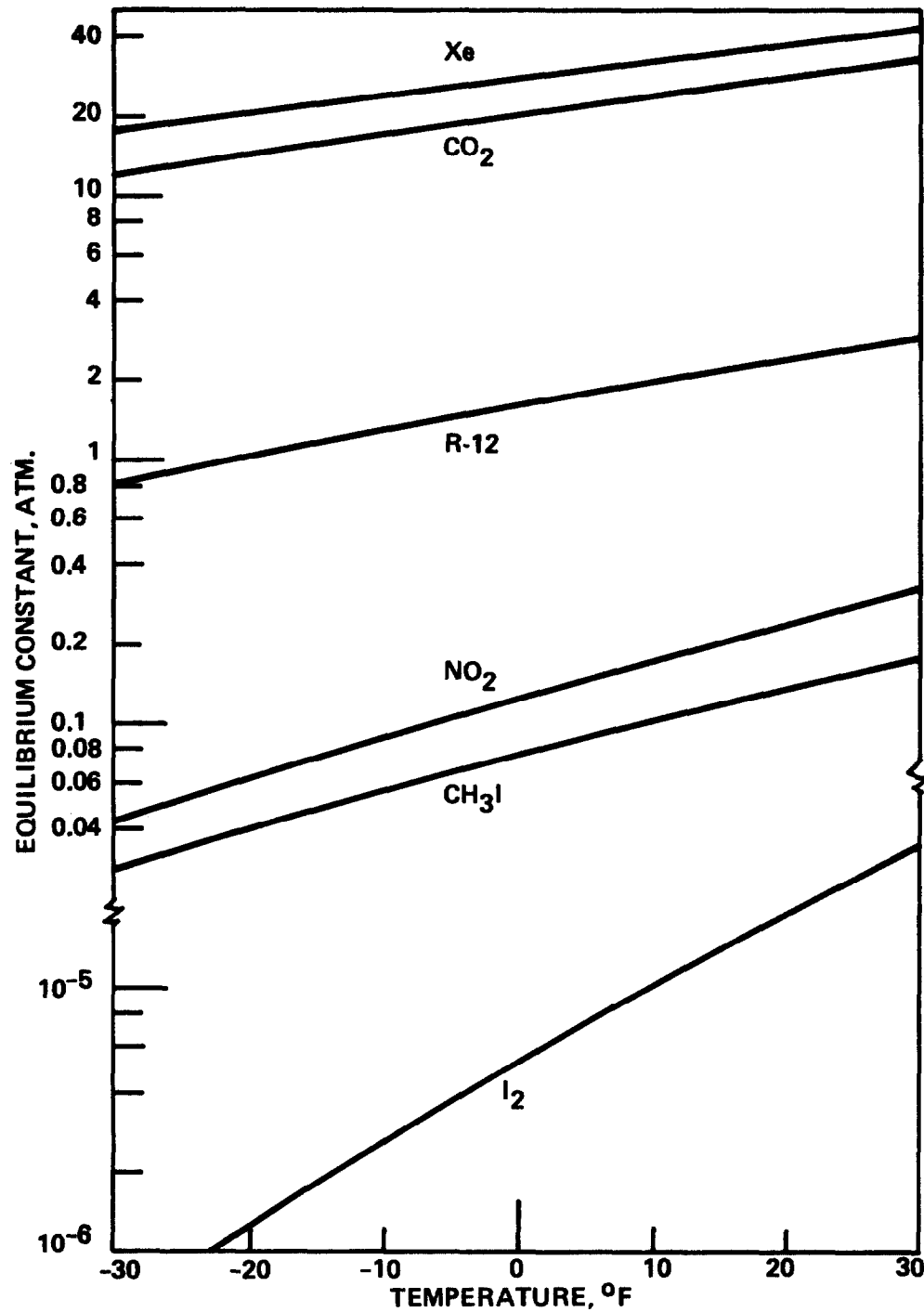


Figure 4. Predicted Distribution Coefficients of High Boiling Feed Gas Components in Refrigerant-12 (CCl_2F_2).

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IV. Pilot Plant Test Results

Krypton absorption data were obtained several years ago and mass transfer correlations developed to describe the absorption phenomena[1,2]. Most of these tests, however, were conducted with a nitrogen feed gas containing only krypton. Recent pilot plant tests have been made with nitrogen feed gases containing (1) 0.1 ppm Kr, (2) 0.1 ppm Kr and, in addition, between 1000 and 3000 ppm CO₂ and between 6000 and 7000 ppm N₂O, (3) 0.1 ppm Kr and no feed gas cooler, (4) 0.1 ppm Xe, and (5) up to 6% carbon dioxide. The results of these tests are summarized in figure 5. Krypton tests were performed with 1 to 1.5 curies of Kr-85 and gamma scintillation techniques were used to analyze krypton process performance. Xenon tests were performed with 1 to 2 curies of Xe-133. Refrigerant-12, carbon dioxide, and nitrous oxide analyses were performed with an in-line infrared analyzer. Oxygen, nitrogen, and refrigerant-12 determinations were made with an in-line gas chromatograph and laboratory mass spectrometer. All tests were conducted at an absorber pressure of 300 psig, temperature between -25 and +10°F, solvent flow of 0.75 or 1.0 gpm, and feed gas flow between 7.5 and 22 scfm.

Pilot plant tests made with only krypton and nitrogen were repeated with high concentration of carbon dioxide and nitrous oxide (N₂O) to identify the effects of these very soluble feed gas components on krypton distribution in the system. The results of these tests suggest that, at least for the absorption step, the presence of other soluble feed gas components has no discernible effect on the process removal of krypton. Of course, the soluble components concentrate with the krypton and thereby dilute the krypton product. This problem, however, is not a very difficult one because the process product flow is only a small fraction of the reprocessing plant off-gas and can be handled in relatively small-scale equipment. Several product purification options are currently being evaluated to separate and isolate the krypton-85 and carbon-14[5].

Hot-gas feed is being considered as an alternative to desublimation of certain feed gas components such as iodine and water in the process gas cooler. In absence of the gas heat exchanger, the bottom of the absorber column will serve as the cooling section for the incoming feed gas and will allow the condensable and desublimable components to pass directly into solution. Comparison of plant tests with and without the feed gas cooler shows that the overall effect of the hot-gas feed on the process performance is small.

Xenon and carbon dioxide removals in excess of 99.99% were measured in pilot plant tests conducted at the same absorber conditions that yielded around 99% krypton removals. Carbon dioxide removals were a little higher than those measured for xenon. This is consistent with component solubilities given in figure 3. Based on pilot plant data, HOG values for Xe and CO₂ were 6 to 10 inches. Significant amounts of carbon dioxide and xenon were found in the recycle solvent for those tests where final stripper molar L/V ratios above 2.0 existed. The absorber performance was noticeably affected by the recycle concentration in those cases where process removals exceeded 99.99%. Substantially better carbon dioxide removals were obtained in runs where higher stripper vapor upflows were maintained.

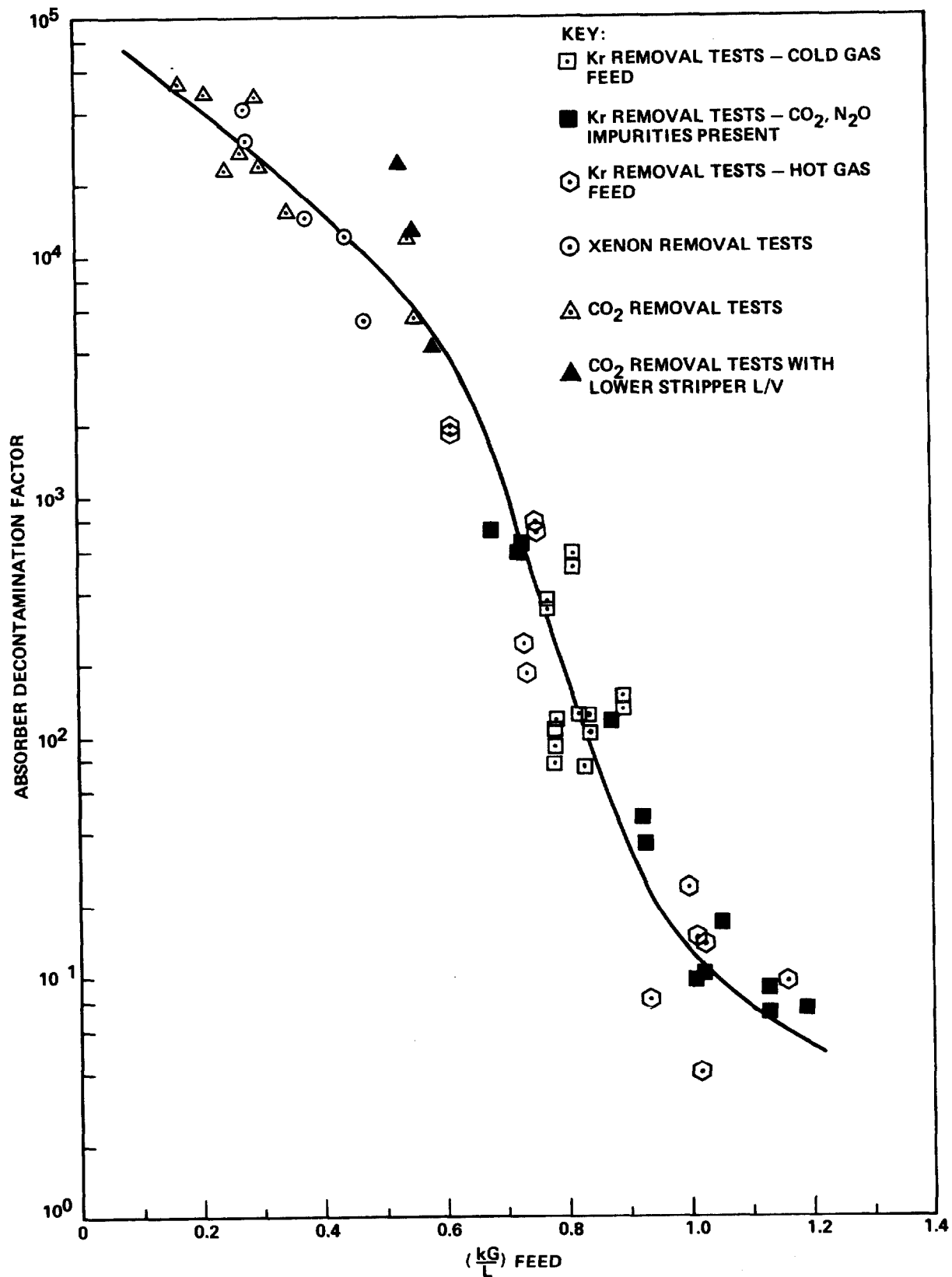


Figure 5. Summary of Pilot Plant Tests with Krypton, Xenon, and Carbon Dioxide

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In these cases, the stripper L/V ratio was near 1.8. At lower stripper boilups, i.e., even when the L/V ratio was as high as 3.0, krypton could not be detected in the recycle solvent. This observation is also consistent with component solubilities.

The results of the pilot plant tests with elemental and organic iodine are summarized in table I. The methyl iodide tests were relatively straightforward to perform and evaluate. A gas mixture was prepared containing CH_3I traced with 5 mc of I-131 and subsequently metered into the absorber feed gas line in the amount necessary to give the desired feed gas composition. No transport problems were evident. Elemental iodine, on the other hand, was difficult to feed and reluctant to move through the feed gas circuit even though the gas lines were heated. For these tests, solid iodine containing 5 mc of I-131 was placed on a finely divided support screen inside a feed cylinder and a pickup sweep gas flow was then diverted through the cylinder and routed to the absorber. Upon contacting the solvent, I_2 became mobile until collected in the solvent still reboiler. Elemental and organic iodine removals in excess of 10^4 were achieved. Gamma scintillation analytical techniques were again used to evaluate process performance. The small amount of activity relative to the plant size and long duration of the tests largely limited the quantitative capability of the counting equipment, since process removals were quite high and the off-gas in most cases contained an undetectable amount of iodine. In some cases, the absorber performance could be calculated from the amount of activity in the recycle solvent by assuming that the absorber off-gas was in equilibrium with the incoming solvent.

The test results clearly show that the efficiency of the process to remove methyl iodide is definitely established by the performance of the solvent purification still. Elemental iodine, on the other hand, was much easier to remove from the recycle solvent. At the conditions of the still, i.e., -10°F , the volatility of refrigerant-12 relative to methyl iodide is 24. This value is greater than 10^5 for elemental iodine. Increasing the reflux ratio in the solvent still from 0.13 to 0.34 (tests 7 and 8) resulted in a significant reduction in the amount of methyl iodide in the recycle solvent and improved the process removal efficiency by a factor of 4. The effect of any recycled iodine on the process removal efficiency could not be determined because the iodine recycle concentrations were below the level of detection. The test data clearly indicate that higher reflux ratios and more rectifying stages will significantly improve the recovery capability of the process. It is important to point out that water and elemental iodine are significantly less volatile than methyl iodide, and consequently, these two components are much easier to remove from the solvent. Therefore, a process designed to achieve a methyl iodide decontamination factor of 10^6 should be capable of even higher elemental iodine and water removals.

The results of the nitrogen dioxide removal experiments are summarized in figure 6. More than 2 months of the recent test series was devoted to studying the long-term process behavior of NO_2 . A spectrophotometric analyzer having the capability of detecting from 1 to more than 6,000 ppm NO_2 was used for direct in-line concentration determinations. Process removal efficiencies between 97 and 99.9%

Table I. Summary of Iodine Removal Tests*

Test Number	Iodine Form	Solvent Recycle	Still Reflux Ratio	Absorber Feed		Measured Decontamination Factor†	Measured Decontamination Factors§
				Gas Concentration, ppm	Decontamination Factor†		
1	I ₂	No	-	~ 0.01	> 10 ⁴	-	-
2	I ₂	Yes	**	~ 0.01	> 10 ³	-	-
3	I ₂	Yes	0.01	~ 0.01	> 10 ⁴	-	-
4	CH ₃ I	No	-	136	> 6 × 10 ⁴	-	-
5	CH ₃ I	Yes	0.01	7	> 2 × 10 ³	1.5 × 10 ⁴	1.5 × 10 ⁴
6	CH ₃ I	Yes	0.34	248	> 2 × 10 ⁴	5.9 × 10 ⁴	5.9 × 10 ⁴
7	CH ₃ I	Yes	0.34	28	> 2 × 10 ³	4.0 × 10 ⁴	4.0 × 10 ⁴
8	CH ₃ I	Yes	0.13	28	> 2 × 10 ³	1.0 × 10 ⁴	1.0 × 10 ⁴

* General Test Conditions: Absorber Pressure, 300 psig; Absorber Temperature, -10°F; Solvent Flow, 1 gallon/minute.

† Based on absorber gas inlet and outlet stream I-131 analysis.

§ Based on absorber gas inlet and recycle solvent stream I-131 analysis and assumption that the absorber off-gas is in equilibrium with the recycle solvent.

** Solvent still partially by-passed.

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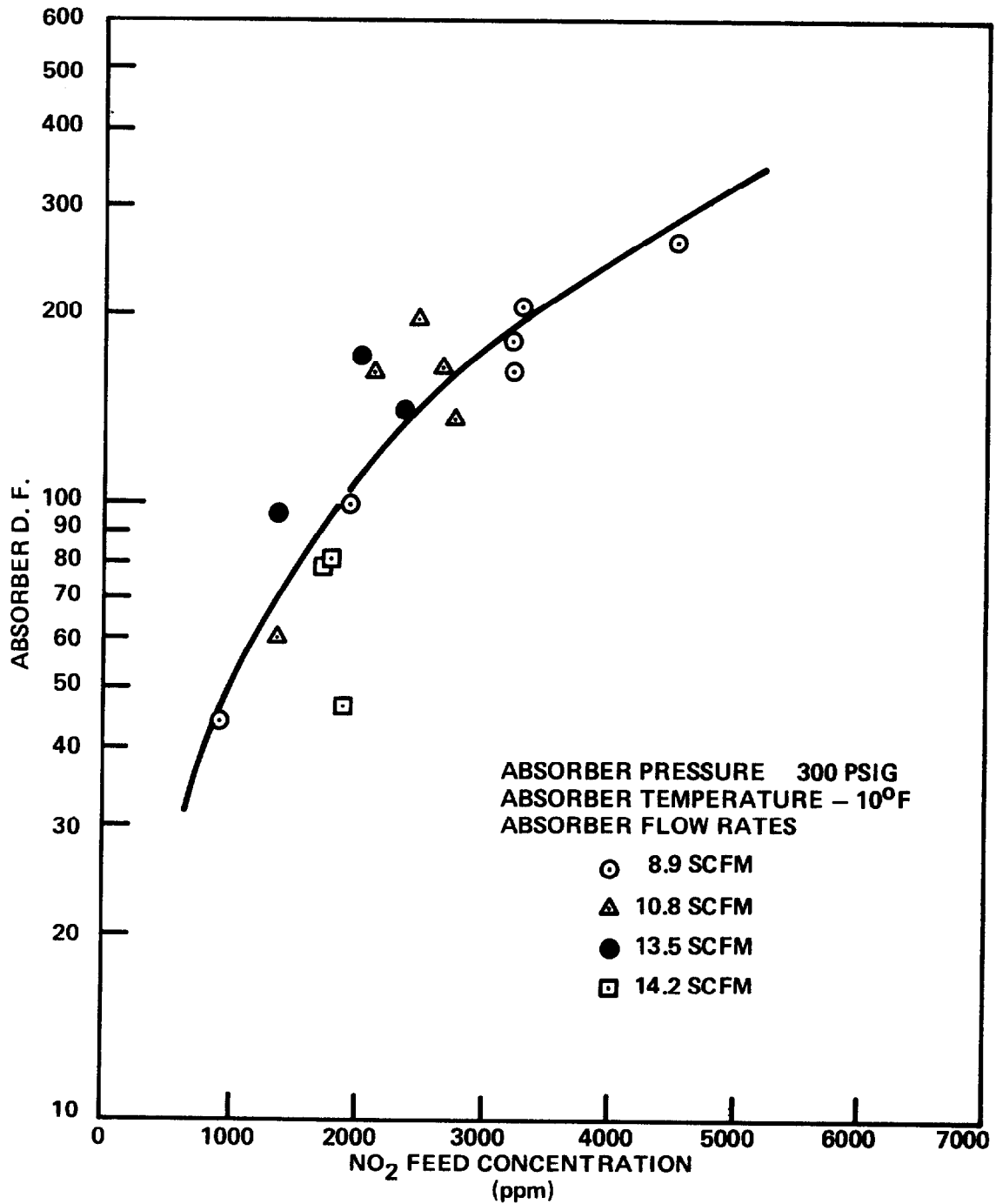


Figure 6. Fluorocarbon Process Removal of Nitrogen Dioxide as a Function of Feed Gas Composition.

were achieved. No feed problems were encountered, and process effects due to the presence of the NO_2 in the feed gas and solvent lines were not observed. The data suggest that the removal of NO_2 is strongly dependent upon the feed concentration. This is contrary to previous experience with the less volatile components, I_2 and CH_3I , and the more volatile components, krypton and xenon. For one series of tests, the concentration of NO_2 in the absorber off-gas remained around 20 ppm regardless of the absorber feed gas flow or inlet concentration. This, of course, again indicates inadequate removal of high boiling components from the recycle solvent. The absorber off-gas concentration did decrease with an increase in the solvent still reflux but not to the extent that was found for the methyl iodide tests. This was not surprising since NO_2 is more volatile than CH_3I and thereby more difficult to remove from the solvent.

Another important part of the overall ORGDP development program is evaluation of process auxiliary subsystems. As part of this work, trapping studies were initiated to evaluate solid adsorbents for removing refrigerant-12 vapor from the process vent and krypton product. The results of these tests are given in table II. An ideal sorbent was identified as one that could reduce the refrigerant concentration in the process off-gas from a nominal 10% to less than 1 ppm. Three sorbent materials were initially considered: 5A molecular sieve, 13X molecular sieve, and H-151 alumina. Tests were conducted with 3-inch-diameter traps filled to a height of 4 feet with the test material. Initial bed temperatures were generally around 70 to 80°F. Tests were conducted with a total gas flow (R-12 and N_2) of 1934 sccm (0.02 ft/sec superficial velocity), 11,670 sccm (0.08 ft/sec), and 120,000 sccm (0.8 ft/sec). The 5A molecular sieve material proved to be unsatisfactory. Trap effluent contained 8.2 ppm before breakthrough, and the sorbent loading was only 0.5% at breakthrough. The alumina bed still could not achieve the desired refrigerant vapor removal. The trap effluent contained 10 ppm before breakthrough and refrigerant loading on the alumina varied between 2.2 and 2.9%. On the other hand, the 13X molecular sieve proved to be an excellent trapping material for the process solvent. The trap effluent contained less than 1 ppm R-12 and the 13X sieve loaded up to 30%. External cooling of the sorbent bed improved the loading capacity of the sieves. Regeneration studies showed that the loaded 13X sieves could be completely regenerated with a 350°F nitrogen sweep flow of 194 lpm in 6 to 7 hours.

V. Solvent Chemistry

The laboratory support work is being performed at ORNL by L. M. Toth, J. T. Bell, and D. W. Fuller. The initial program is designed to evaluate distribution coefficients of the various feed gas components in refrigerant-12, look at component interactions in a multicomponent system, and identify possible corrosion conditions that could develop. Undoubtedly, this important effort will be expanded as the program progresses. Work in this area was only initiated recently but a substantial amount of data has already been obtained. Several aspects of the physical and chemical behavior of I_2 in R-12 have been examined by absorption spectrophotometry in a high pressure optical cell. Iodine in R-12 has an electronic absorption band in the visible light region at 520 nm arising from a solvated I_2 molecular species.

Table II. Summary of R-12 Adsorption Studies for the Product Purification and Solvent Recovery Subsystems

Test Number*	Adsorbent	Cycle	Total Feed Flow, sccm	Feed Composition, % R-12	Bed Temp., °F		Breakthrough Time hr	R-12 in Effluent Before Break, ppm	Regeneration Scheme	
					Initial	Final			Temp., °F	Time, hr
1	5A Sieve	1	1,934	9.5	65	65	0.45	8.2	375	2.2
2	H-151 Alumina	1	1,934	9.5	75	75	2.50	10.1	440	3.6
3	H-151 Alumina	2	1,934	9.5	69	69	2.00	10.7	430	1.7
4	H-151 Alumina	3	11,670	10.0	77	88	0.30	19.0	420	1.5
5	13X Sieve	1	1,934	9.5	75	98	19.50	< 1	375	4.0
6	13X Sieve	2	11,670	10.0	78	127	2.67	150**	330	6.0
7	13X Sieve	3	11,670	10.0	85	139	2.67	< 1	350	7.7
8	13X Sieve	4	11,670	10.0	68	86††	2.92	< 1	360	6.5
9	13X Sieve	5	1.2×10^5	3.1	73	85††	1.17	< 1	350	6.0
10	13X Sieve	6	1.2×10^5	3.1	73	87††	1.12	< 1	360	6.0
11	13X Sieve	7	1.6×10^5	2.3	88	145	0.5	< 1	360	6.0
12	13X Sieve	8	1.6×10^5	2.3	75	113††	0.7	< 1	340	6.0

* All tests except 11 and 12 conducted at 4.5 psig in a nominal 3-inch-diameter trap with 0.0513 ft² (47.6 cm²) cross section. Tests 11 and 12 were made at 21 psig.

† The bulk gas is nitrogen.

‡ R-12 loading defined as [(1b R-12 adsorbed)/(1b adsorbent)] × 100.

** The previous regeneration of 375°F for 4 hours was not sufficient to regenerate the 13X sieve loaded during the previous test; hence, the high concentration of R-12 in the effluent.

†† These tests conducted using external bed cooling.

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In the absence of any added water, dilute solutions of iodine in refrigerant-12 are not expected to chemically react with either the solvent or stainless steel containment. There is some indication, however, that refrigerant-12 solutions of iodine containing excessive amounts of free water might interact with stainless steel. The solubility and distribution coefficient of iodine is currently being measured as a function of temperature. Later, the solution effects of free water will be determined.

VI. Conclusions

Recent and more detailed pilot plant tests continue to support hypotheses drawn from earlier scoping tests and performance calculations[1]. In short, the fluorocarbon-based process is versatile, has a high tolerance for feed gas impurities, and can function in a multiplicity of ways to clean up reprocessing plant off-gas and isolate the many contaminants for long-term storage and disposal. Tests show that a process designed to remove krypton-85 and carbon-14 can also achieve high iodine, methyl iodide, water, and nitrogen dioxide decontaminations. A comprehensive pilot plant testing program and an exhaustive solvent chemistry laboratory effort are continuing to fully define the capability and limitations of the FASTER process. If the process development program proceeds according to schedule, sufficient information will be available within 3 years to begin final design of an LMFBR or LWR demonstration plant. So far, no detrimental effects due to the presence of the various feed gas components in the fluorocarbon process have been uncovered except maybe a possible corrosion problem that could develop in a stainless steel system if free water is present. Materials of construction will be selected after the solvent chemistry work has been completed and possible corrosion mechanisms identified. Substantially more testing is required at this point before the process can be fully evaluated.

VII. References

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DISCUSSION

GRADY: How much additional research and development is required before the FASTER process will be sufficiently developed to design a commercial fuel reprocessing plant?

EBY: We feel that within three years, we will have sufficient design and application information to begin the design of a facility for a commercial fuel reprocessing plant.

STUART: What is the anticipated krypton content coming from the stripper?

EBY: The pilot plant is designed to achieve a krypton factor between 10^4 and 10^5 .

STUART: What would that be in terms of what percentage of krypton in the total gas stream?

EBY: From 10-50%.

R. A. BROWN: You mentioned limitations. What do you consider to be the major limitations of a fluorocarbon absorption process?

EBY: That is what we are trying to find out right now.

R. A. BROWN: Do you now anticipate any serious limitations?

EBY: We are presently working on a solvent chemistry program and we are studying solubility limitations and possible corrosion effects. This may be a problem, but right now we don't know. We think it is a very versatile process.

MURBACH: What are you going to do with the absorbed NO_2 ?

EBY: The NO_2 collects in the solvent still reboiler, and then, depending on its concentration, can either be recycled back to the dissolver or disposed of.

VAN BRUNT: What is the rate of radiolytic decomposition of the solvent?

EBY: G values have been measured from Refrigerant-12 and are around four. We don't consider this important as the quantities will be small and the principal decomposition products will be R-113, R-114, which will collect in the solvent still reboiler.

VAN BRUNT: Do you foresee any significant hydrochloric acid formation?

EBY: This may be possible. We don't consider this a problem though.

SKOLRUD: In regard to solvent cleanup applications of the FASTER process, what is proposed for recovery and final conversion

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of absorbed iodine and organic iodides?

EBY: These components will collect in the solvent still
reboiler along with the NO_2 and will be reacted to a suitable solid
form for storage.

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HTGR-REPROCESSING OFF-GAS CLEANING BY THE AKUT-PROCESS

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Abstract

During reprocessing of HTGR-fuel the graphite matrix has to be removed in order to gain the heavy metal, which is accomplished by burning the crushed fuel elements. During the burning part of the krypton and tritium is released from the fuel. Since the combustion gas is a mixture of CO_2 and O_2 , the burner off-gas consists mainly of CO_2 with a small amount of CO and fission products, mainly in gaseous form but also aerosols.

A facility, called AKUT II, which consists of the following process steps

- aerosol removal by electrostatic precipitators followed by HEPA-filters
- catalytic conversion of CO and O_2 to CO_2
- compression and liquefaction
- separation of krypton by distillation
- adsorption of tritiated water on molecular sieve

is now being installed in the KFA hot cells. The facility will be ready for cold operation early in 1977. After start-up of the HTGR-reprocessing pilot plant JUPITER the off-gas from the head-end will be treated in the AKUT facility.

Introduction

Hot tests with a smaller facility - AKUT I, throughput $1\text{--}3 \text{ m}^3/\text{h}$ STP - were carried out in 1974. A review of those tests and of preliminary cold tests has been presented at the 13th USAEC Air Cleaning Conference [1]. Experience with the AKUT I facility has led to the construction of an improved and scaled-up AKUT II facility with a throughput of $10\text{--}20 \text{ m}^3/\text{h}$ STP. Extensive tests with simulated off-gas are planned before the AKUT facility will be connected to the JUPITER pilot plant.

In the JUPITER head-end the AVR fuel elements, which contain (U/Th) O_2 fuel particles, will be crushed and burned in a fluidized bed burner, which will be operated with a $\text{CO}_2\text{--O}_2$ -combustion gas. In steady state the off-gas will contain ~ 90 % CO_2 , ~ 10 % CO, nil O_2 , ~ 1 ppm Kr, and ~ 1 ppb T. Since the burner is operated at low pressure, inleakage of air from the cell atmosphere may result in small amounts of O_2 and N_2 in the off-gas. CO and O_2 are converted to CO_2 in a catalytic burner. The off-gas is then compressed, condensed and distilled to produce both a krypton-rich product stream and a purified liquid stream. The distillation will be operated at temperatures between 0 °C and 20 °C at the column inlet and pressures between 35 and 100 bar, depending on the amount of light gases whose behavior in the distillation column needs to be further investigated. According to MERZ et al. [2] it is expected that krypton is concen-

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trated faster at the top than the light gases. The tritium - in the form of tritiated water - leaves the column with the bottom stream from which it is removed by molecular sieve.

Facility description

Simplified process flowsheet

The AKUT II flowsheet is shown schematically in Figure 1. The feed gas - from gas cylinders or, in a later phase, from the JUPITER facility - enters at room temperature. During cold tests the electrostatic precipitators (EF 1 and EF 2) are not needed and are bypassed. During hot tests one precipitator is in use while the other one is cleaned with water and afterwards dried by heating the outside and purging with CO₂. Figure 2 shows the electrode, the casing with the heating elements and a completely assembled precipitator. The precipitators and the tank for the wash water are placed in a shielded (50 mm lead) air tight box in which a low pressure of 10 mm H₂O is maintained. The box for the HEPA-filters FF 1 and FF 2 is also kept at low pressure but is not shielded, because in earlier hot tests [1] it was found that practically all aerosol activity was removed by the electrostatic precipitator.

After the filter step the off-gas is fed into the catalytic converter system, in which by means of the blower K 2 so much CO₂ is constantly recycled that even an off-gas consisting of 100 % CO is sufficiently diluted that it can be converted to CO₂ without damaging the catalyst CTK 1 or reaching the explosion limits of a CO₂-CO-O₂-system. The reaction heat is removed by water cooler WT 1. The recycle gas remains at the working temperature of the palladium catalyst, so that the electrical heating is only needed for start-up or to make up for heat losses of the gas to the environment. Behind the entrance point of the off-gas into the recycle stream the CO and O₂ contents of the recycle stream are measured. Utilizing these data the control valves for additional CO or O₂ are operated. After the catalytic conversion the gas should not contain more than 0.1 % O₂ or CO.

When the gas leaves the converter it is cooled to ambient temperature in heat exchanger WT 2. It is then fed to the three stage piston compressor K 4. The compressed gas is cooled and condensed in the main compressor surge tank TK 1, which is water cooled, and the heat exchanger WT 4, which is cooled by refrigerant (a silicon oil) of - 30 °C from the refrigeration unit. Tank TK 1 is designed to hold the entire liquid charge of the high pressure part of the facility without need for cooling.

The liquefied gas is fed into the distillation column. The column has an inner diameter of 40 mm and a height of 5.4 m without condenser and reboiler. The maximum height of the column was predetermined by the space available in the hot cells. The column has 5 gas-liquid sampling points (Figure 3) and 4 sections of packing (wire spirals 4 x 4 mm, Figure 4) between the samplers. Column performance has been tested with air and water. Figure 5 shows generalized flooding curves: No. 1 for the wire spirals, determined with air/H₂O; No. 2 for Goodloe packing, determined with CO₂/CO₂ (according to ORNL data [4]); No. 4 for the samplers, determined with air/H₂O and No. 3 gives the calculated values for wire spirals and

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Goodloe packing, where

u_m	= superficial gas velocity	m/s
ρ_g and ρ_L	= gas and liquid density	kg/m ³
μ_L	= liquid viscosity	cP
L and G	= liquid and gas mass	kg/h
g	= gravitational constant	m/s ²

The samplers, except the ones at top and bottom, can also be used as feed points, so that the most advantageous feed point can be determined.

The reboiler has two capacitance type liquid level probes and is flanged with a 5 kW electrical immersion heater. The condenser is of annular shell-and-tube construction with the process fluid on the shell side. The internal volume is reduced by use of a displacement body. Refrigerant enters through the upper cap via three tubes. The three refrigerant coils are arranged in three coil banks. The three tubes leave the lower cap separately and exit on a common header. Should any O₂ or CO accumulate at the top of the condenser, it can be withdrawn and fed back into the surge tank NDB 1 before the catalytic converter.

The product from the top can be withdrawn in liquid or gaseous form. It is pumped into cylinders at a maximum pressure of 150 bar at ambient temperature.

The purified liquid from the bottom is heated in heat exchanger WT 6 and expanded to 20 bar. Before expansion to atmospheric pressure tritium absorbers (Figure 6) are intended to be put in. The gaseous CO₂ which contains traces of tritiated water is fed to absorber I while the second one is regenerated with hot CO₂. The hot regeneration gas is cooled to ambient temperature. The water condenses and flows into waste tank WTK. The regeneration gas is reintroduced into the burner off-gas. The purified off-gas from absorber I is then used to cool the regenerated absorber II and is then expanded to atmospheric pressure and, after passing a HEPA-filter, is released to the atmosphere. Laboratory tests have shown that at 20 bar and 0 °C and a gas velocity of 0.05 m/s 1000 g ⁴ Å molecular sieve will absorb 160 g H₂O. For regeneration ~ 0.9 m³ CO₂ per kg molecular sieve will suffice. This type of molecular sieve has already be tested for tritium removal in earlier hot tests [3].

The tritium absorption system is scheduled to be designed this year and to be put into the facility in the first half of 1977.

Sampling and analysis

System variables such as temperature, pressure, flowrate and concentrations at some points (e.g. in-line Kr-monitoring at column entrance, top, and bottom; O₂ and CO concentrations in the catalytic converter etc.) are necessary for process control and are routinely measured. Additional data, which are necessary for quantitative treatment of experimental results, are made available by drawing gas and liquid samples from the column, the top and bottom streams and several tanks. The concentration of ⁸⁵Kr is measured with beta scintillation cells. For nonradioactive components of the samples, a mass spectrometer will be used. This instrument is capable of

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detecting atomic mass units in the range 2 to 300 and trace impurities in gases down to 2 ppm.

Facility control

The facility has a main control panel, a sampling station, which contains instruments and manually actuated solenoid valves needed for sampling, and a transmitter station. The refrigeration unit has its own small control panel.

Status of the facility installation

As was mentioned before the facility is now being installed in the KFA hot cells on the roof of the hot cell row in which the JUPITER facility is housed. The catalytic converter is the first unit to be tested. It was mounted in a rack and was transported to the hot cells as a complete unit. It is now being connected to the main control panel and as much piping as is necessary for the separate testing of this unit is being fitted. Function tests of the catalytic converter are scheduled for August 1976.

The condenser and reboiler will be welded to the column in August. The complete column will be placed in a rack in the machine shop. Into this rack the boxes with the electrostatic precipitators and the HEPA-filters will later on be mounted. They are not needed for the preliminary cold tests. All parts have been delivered and the final assembling is scheduled to begin in September 1976. Cold tests are expected to start in February 1977.

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- [2] E. Merz et al.:
"Verfahren zum Abtrennen von Krypton aus einem bei der Verbrennung graphithaltiger Kernbrenn- und/oder -brutelemente anfallenden Abgas".
DP 24 37 810.
- [3] H. Beaujean et al.:
"Reinigung der Verbrennungsabgase bei der Wiederaufarbeitung von HTR-Brennelementen".
JÜL-925-CT (1973).
- [4] R. W. Glass et al.:
"Development of the Krypton Absorption in Liquid Carbon Dioxide (KALC) Process for HTGR Off-Gas Reprocessing".
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AKUT - II
Flowsheet

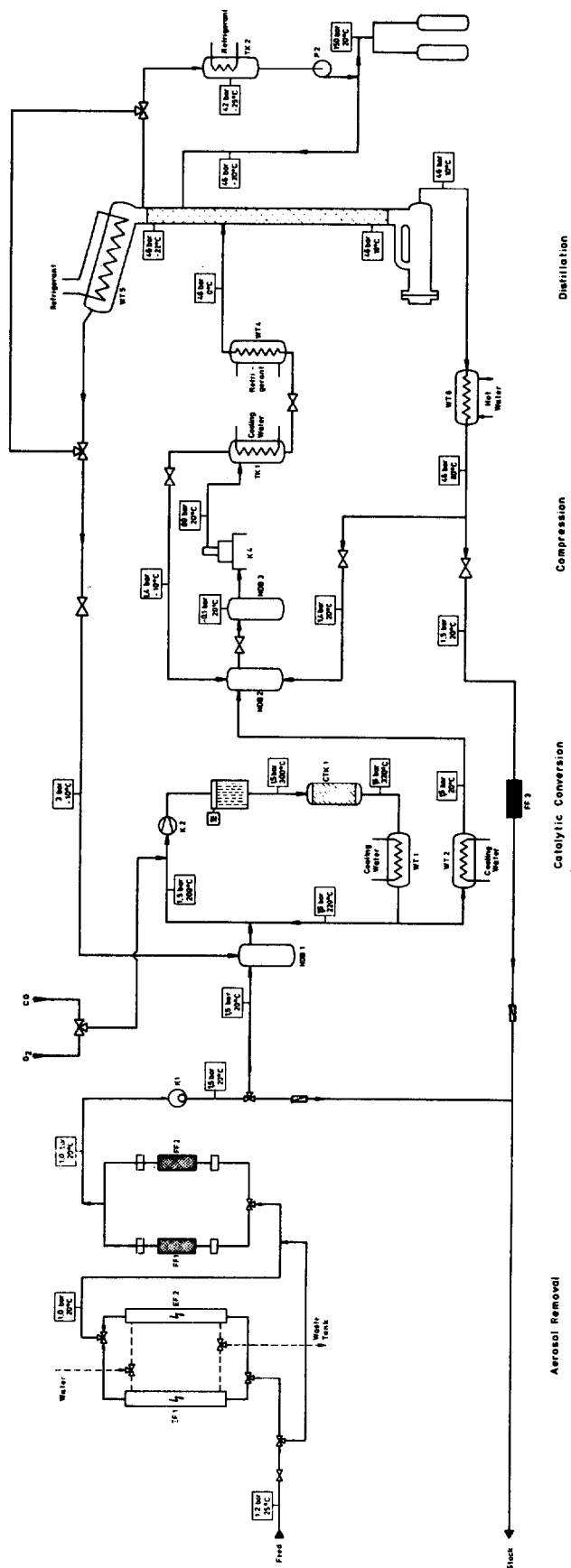


Figure 1: Simplified flowsheet of the AKUT II facility

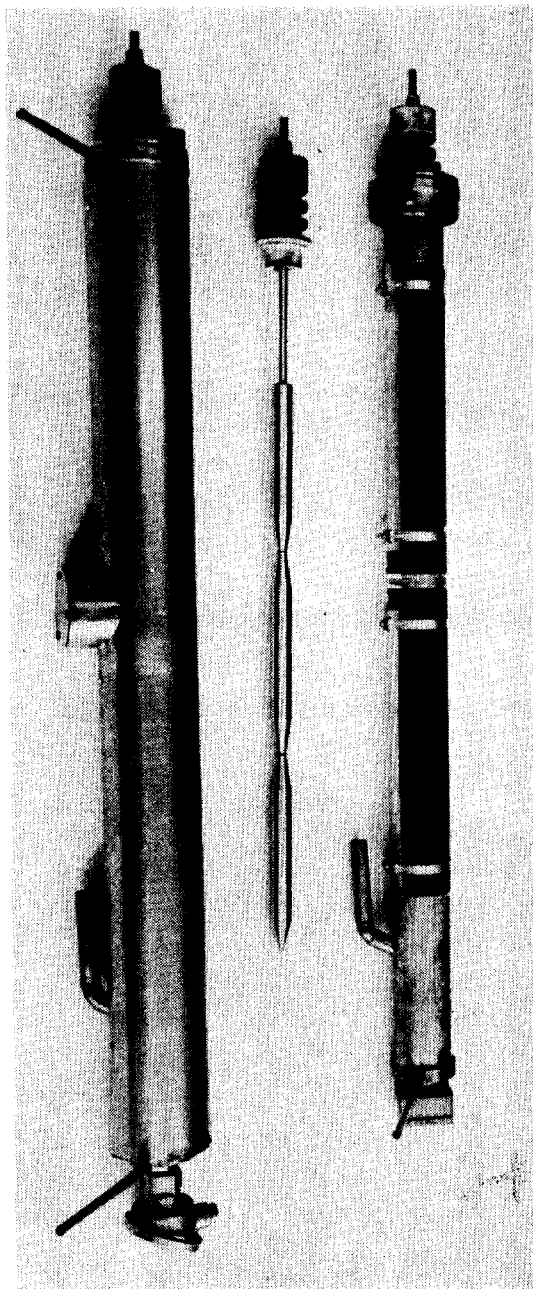


Figure 2: Electrostatic precipitator

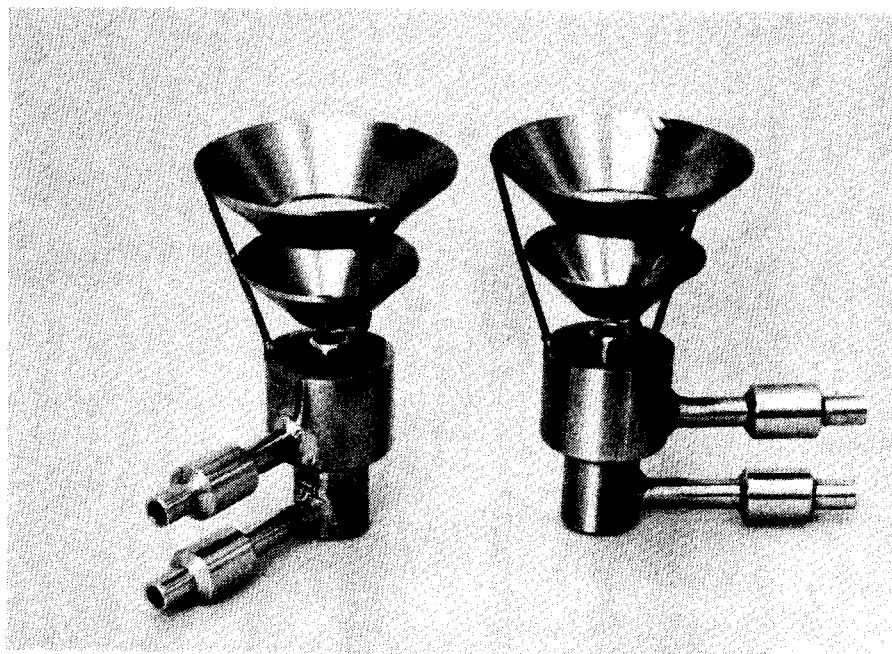


Figure 3: Gas-liquid samplers in the distillation column

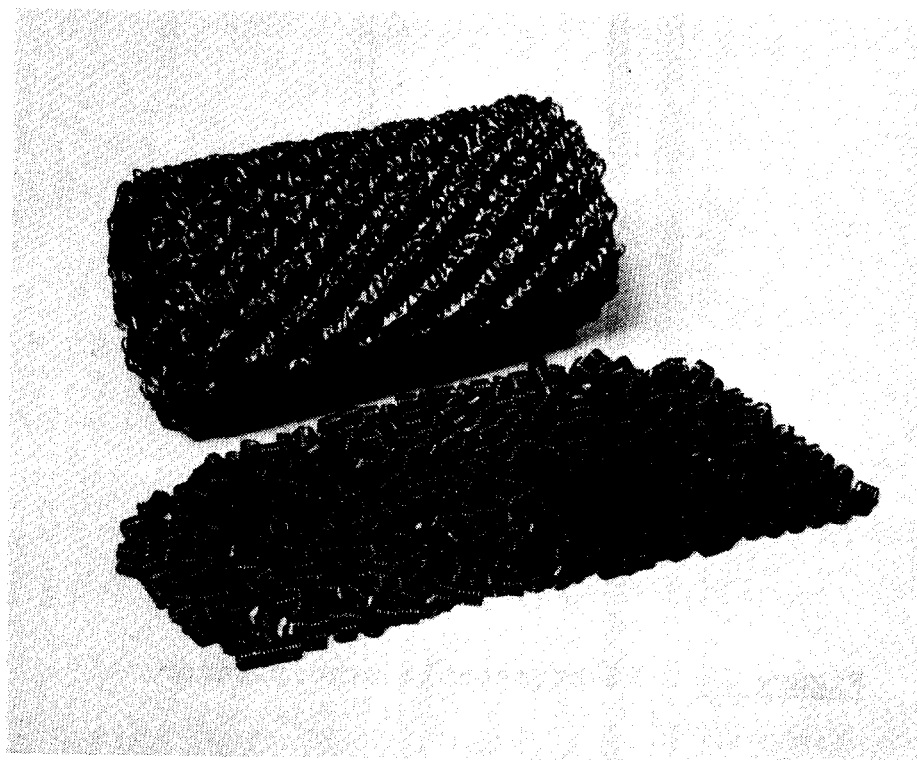


Figure 4: Packings
Goodloe packing (top)
wire spirals 4 x 4 (bottom)

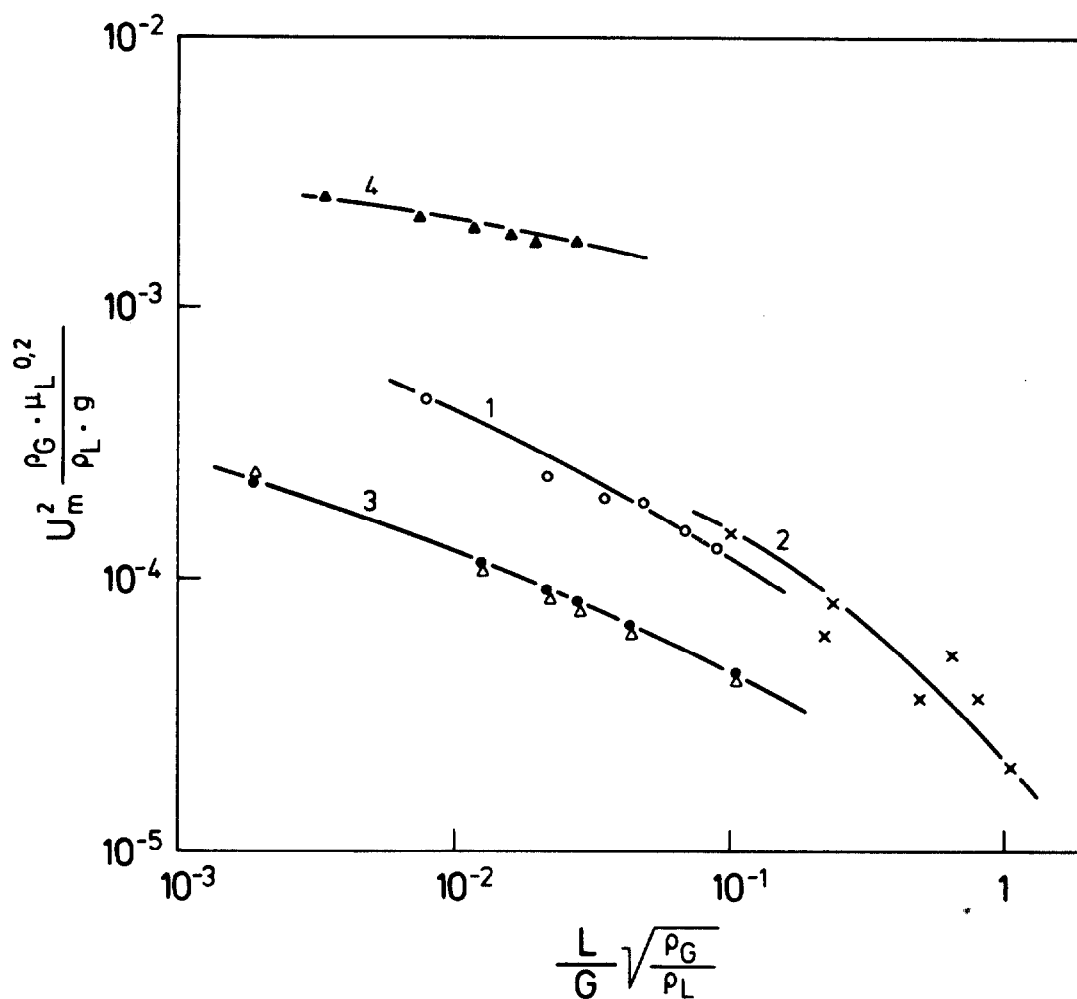
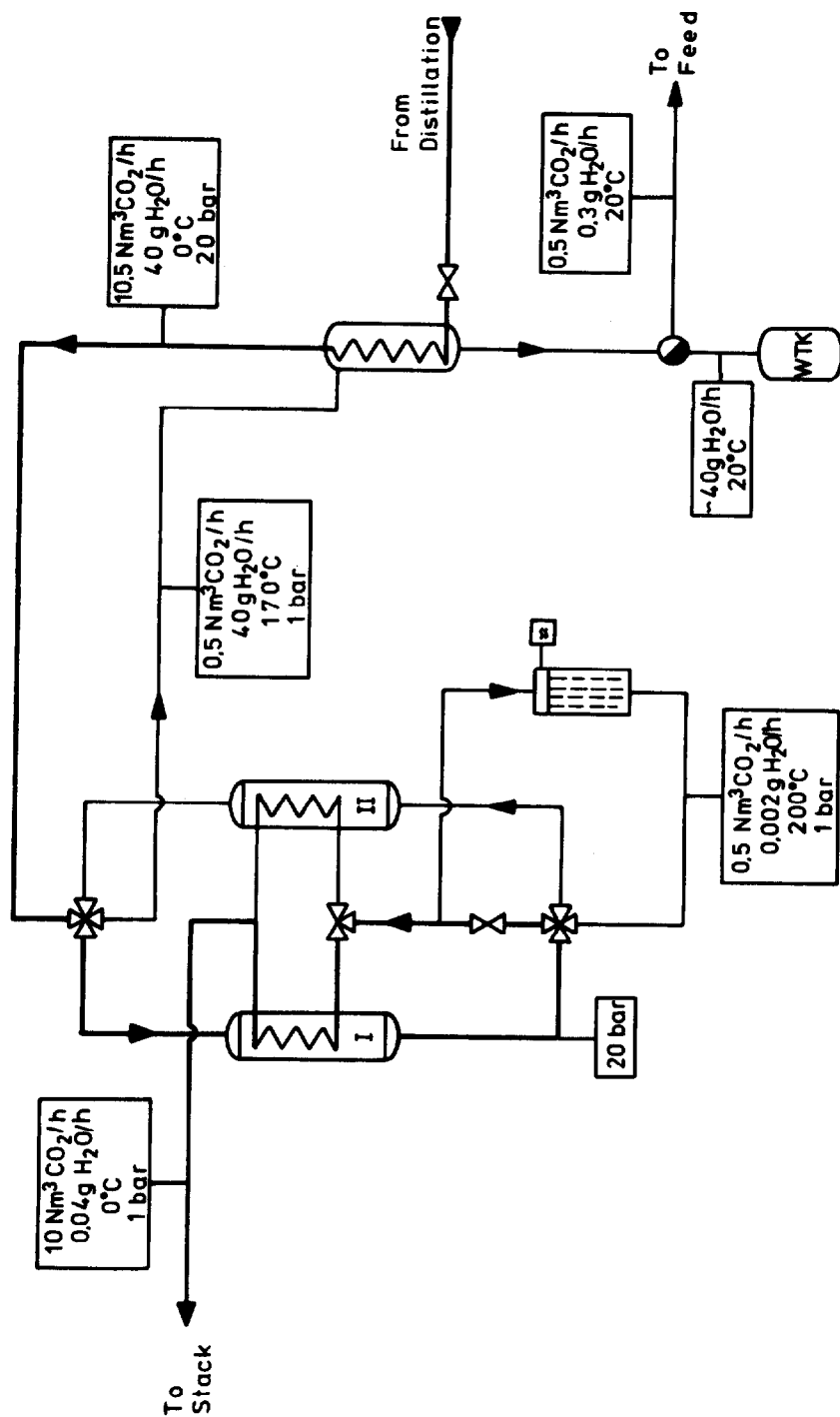


Figure 5: Flooding curves for packed columns

- 1) Braunschweiger Wendeln 4 x 4
(wire spirals), system air/H₂O
- 2) Goodloe packing, system CO₂/CO₂ (ORNL-data)
- 3) Calculated values for 1) and 2)
- 4) Gas and liquid samplers in the column,
system air/H₂O



AKUT II Tritiumremoval

Figure 6: Schematic flowsheet of the tritium removal system for AKUT II

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DISCUSSION

DEMPSEY: The paper did not mention ^{14}C . Will this radionuclide be removed by AKUT-2?

BOHNENSTINGL: Carbon 14 is a problem in this process. Some work must be done on a fuel fabrication program to remove or separate carbon 14 dioxide from other gases.

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EXPERIMENTAL STUDIES ON THE KRYPTON ABSORPTION IN LIQUID CO₂ (KALC) PROCESS*

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Abstract

Results are presented for a series of experiments to quantify krypton removal from simulated High-Temperature Gas-Cooled Reactor reprocessing off-gas by the KALC process. The Experimental Engineering Section Off-Gas Decontamination Facility used in the campaign provides engineering-scale experiments with nominal gas and liquid flows of 5 scfm and 0.5 gpm respectively.

Equilibrium and nonequilibrium mass transfer experiments for the CO₂-O₂-Kr system are described. Data analysis indicates values of HTU for krypton on the order of 0.5 ft for decontamination factors from 100 to 10,000. Recent flooding information for the packed columns is combined with previous data and is shown to be well represented by an empirical flooding equation.

Introduction

As part of the Thorium Utilization Program developmental work being carried out at the Oak Ridge National Laboratory, the Experimental Engineering Section Off-Gas Decontamination Facility⁽¹⁾ (EES-ODF, see Fig. 1) has been operated to quantify the absorption of krypton by liquid CO₂. The work presented here comprises approximately 30 experiments involving the mass transfer of krypton into liquid CO₂ in the presence of O₂ and 10 experiments in which conditions within the packed absorption column were chosen such that CO₂-Kr equilibrium values were obtained as a check on values of equilibrium data reported in the literature.^(2,3) Additional column flooding data are also presented and compared with previous values.⁽¹⁾

*Research sponsored by the Energy Research and Development Administration under contract with Union Carbide Corporation Nuclear Division.

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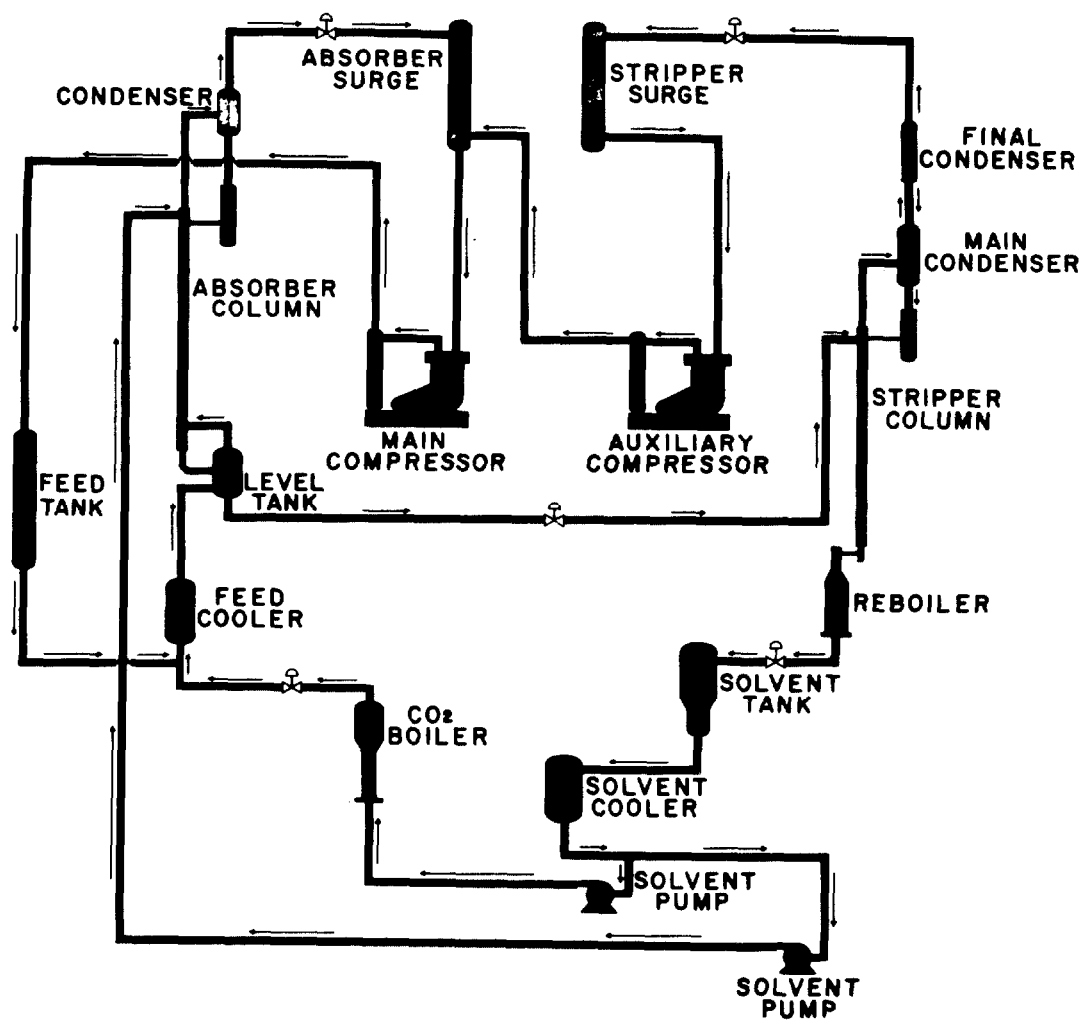


Fig. 1. Experimental Engineering Section Off-Gas Decontamination Facility.

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Flooding Studies

Fluid dynamic data for the EES-ODF packed columns have been reported.⁽¹⁾ More recently, a few additional experiments with the liquid CO₂ system were conducted during a High-Temperature Gas-Cooled Reactor (HTGR) campaign in the Oak Ridge Gaseous Diffusion Plant (ORGDP) facility for off-gas decontamination studies.⁽⁴⁾

Figure 2 presents the collective flooding information obtained for the packed columns investigated. Included in the data shown in this figure are flooded conditions found for the 1-1/2-in. absorber column and the 3-in. stripper column in the EES-ODF, together with the more recent data (darkened points) acquired from operation of the 3-in. fractionator column in the ORGDP facility. All columns are packed with presized canisters (6 in. long) of Goodloe* wire mesh packing.

The flooding curve is presented in a standard form for the particular packing (i.e., no "packing factor" is included in the ordinate grouping). The following quantities are noted for Fig. 2:

$$\begin{aligned} L &= \text{liquid flow rate, lb/ft}^2 \cdot \text{hr,} \\ G &= \text{gas flow rate, lb/ft}^2 \cdot \text{hr,} \\ \rho_G &= \text{gas-phase density, lb/ft}^3, \\ \rho_L &= \text{liquid-phase density, lb/ft}^3, \\ \mu_L &= \text{liquid-phase viscosity, cP,} \\ U_M &= \text{gas velocity at flooding, ft/sec,} \\ g &= 32.2 \text{ ft/sec}^2. \end{aligned}$$

With the addition of the four experimental points from the ORGDP fractionator, a curve has been fitted to all points shown. The results are as follows:

$$\bar{y} = a + b\bar{x} + c\bar{x}^2 = \log(y), \quad (1)$$

where

$$\begin{aligned} \bar{x} &= 2.0 + \log(x), \\ y &= \text{ordinate values of } \frac{U_M^2 \rho_G \mu_L^{0.2}}{g \rho_L}, \\ x &= \text{abscissa values of } \frac{L}{G} \sqrt{\frac{\rho_G}{\rho_L}}, \\ a &= -3.44748, \\ b &= 0.379889, \\ c &= -0.315457. \end{aligned}$$

* A product of the Packed Column Co., a Division of Metex Corp., Edison, N.J.

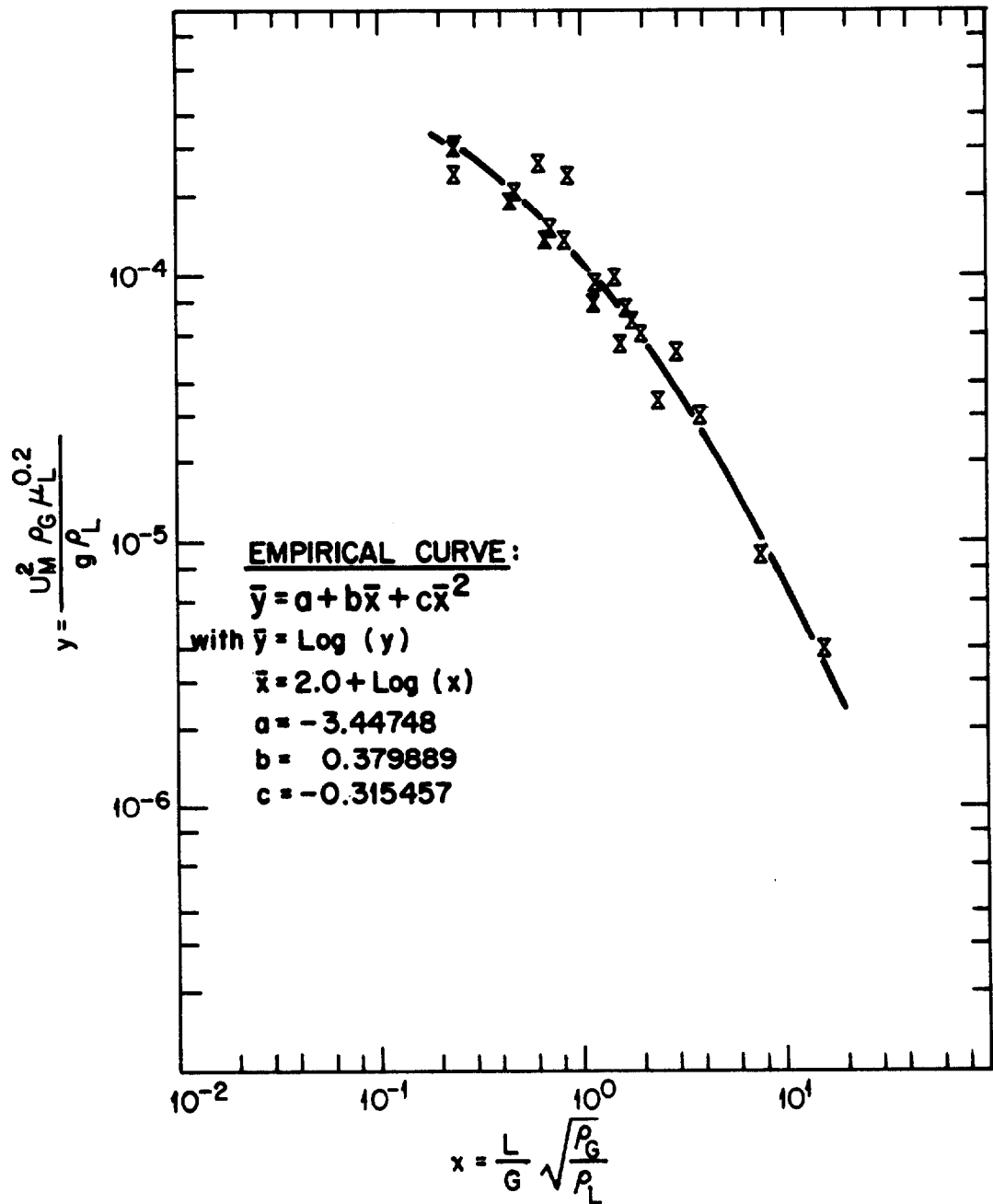


Fig. 2. Curve constructed by using collective flooding information.

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Practically all of the fluid dynamic experiments represented by the flooding curve have involved CO_2 only (i.e., both gas and liquid phases are essentially pure CO_2). The effect of light gases such as O_2 , N_2 , etc., is not experimentally implicit. However, most of the areas of concern in the KALC process involve pure CO_2 . The capacity or throughput of the packing at flooding is less than that suggested in literature supplied by the vendor (overall, by perhaps 50% depending on conditions). The pressure drop at flooding is approximately 0.5 in. H_2O per foot of packing.

Equilibrium Operations

At the beginning of the present work, it was recognized that a fundamental question concerning Kr- CO_2 equilibrium existed. The problem can be explained by referring to Fig. 3. Two independent sets of equilibrium data^(2,3) for the same system were available, and these were not in agreement. The data are expressed as the equilibrium ratio y/x , where y and x denote krypton concentrations in the vapor and liquid CO_2 phases, respectively. Calculations based on each set of data produce widely varying results.⁽⁵⁾ Moreover, decisions as to what experimental conditions to use for the present work depended on the value of the Kr- CO_2 equilibrium ratio. Thus a series of experiments was conducted early to determine whether the dilemma could be resolved.

Two important considerations are worth noting. First, the EES-ODF is not designed to provide equilibrium data per se. Since the facility involves equilibrium in an indirect manner, it is a question of precision regarding the worth of equilibrium observations. Second, the degree of accuracy relative to sampling and analysis is very difficult to establish, especially in limited-time operations. Consequently, the objective of the equilibrium studies was to present evidence as to which set of equilibrium data was more nearly accurate. The studies also allowed a pseudo-quantitative evaluation of sampling and analytical techniques for the EES-ODF. Details of the sampling, monitoring, and analytical techniques for the EES-ODF are presented elsewhere.^(1,6)

Table 1 presents the basic data for the ten equilibrium experiments. The method of operation during these experiments was straightforward. The facility was operated with varying amounts of oxygen, at different pressures and temperatures, but always with the liquid-to-vapor flow ratio in the absorber column set to produce a "pinched" condition at the bottom of the packed section. A pinched condition results when the liquid-to-vapor ratio is less than the equilibrium ratio (y/x), given sufficient packed section length. The result of operating in a pinched mode is that the vapor entering and the liquid leaving the column will be essentially in equilibrium.

Table 2 summarizes the equilibrium experiments with regard to the facility method of operation. After sufficient time had been allowed for system transients to subside in each run, both the gas and the liquid at the bottom of the packed section were sampled and analyzed for krypton and O_2 . Calculated values given in Table 1 are based on the CO_2 - O_2 -Kr equilibrium model described in ORNL/TM-4947.⁽⁷⁾ The equilibrium model assumes the validity of the data of Notz et al.⁽³⁾ for krypton. Figures 4 and 5 present the computer model results for the equilibrium ratio and Henry's constant for the various components.

Figure 6 presents summary results of the equilibrium studies. Values of y and x (mole fraction) for krypton were determined by sampling and analysis, and

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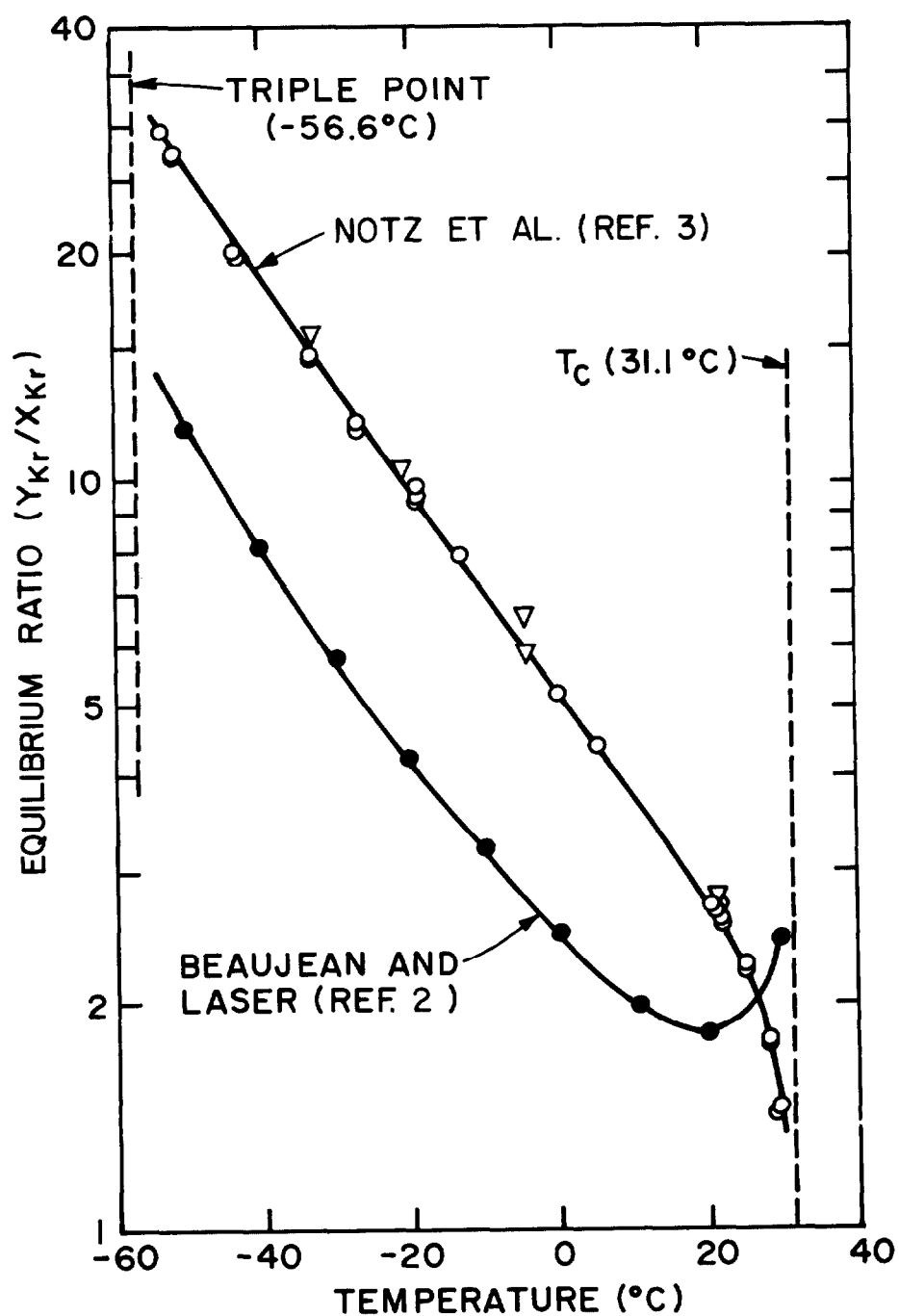


Fig. 3. Comparison of Kr-CO₂ equilibrium ratios from two independent sources.

Table 1. Summary of results obtained in ten equilibrium experiments in the EES-ODF

Experiment number	Pressure (psig)	Temperature (°C)	Y _{O2}		(y/x) _{Kr}	
			Measured	Calculated ^a	Measured	Calculated ^a
232	340	-17.5	0.0770	0.1005	6.94	7.74
241	254	-28.5	0.1510	0.1537	9.02	10.23
254	375	-12.1	0.0790	0.0534	6.90	7.00
268	309	-18.5	0.0338	0.0579	8.31	8.49
275-A	338	-13.5	~0	0.0103	7.17	7.75
275-B	280	-19.6	~0	0.0130	8.72	9.33
275-C	286	-19.4	~0	0.0238	9.75	9.14
275-D	218	-27.3	~0	0.0202	11.81	11.82
275-E	290	-19.0	~0	0.0245	7.90	9.02
296	290	-25.7	(0.1180)	0.1738	8.85	9.03

^aCalculations were based on the CO₂-Kr-O₂ model presented in ORNL-TM-4947. (7) The (y/x)_{Kr} ratio was calculated assuming the validity of the data of Notz et al. (3)

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Table 2. Summary of experimental equilibrium operations

Experiment number	Description of operation
232	Typical mass transfer experiment involving both gas and liquid countercurrent operation with a low value of liquid-to-vapor ratio
241	Similar to 232
254	Similar to 232
268	Similar to 232
275-A	Only liquid flow in operation; equilibrium with overgas achieved by long-term system operation
275-B	Similar to 275-A
275-C	Similar to 275-A
275-D	Similar to 275-A
275-E	Similar to 275-A
296	Similar to 232

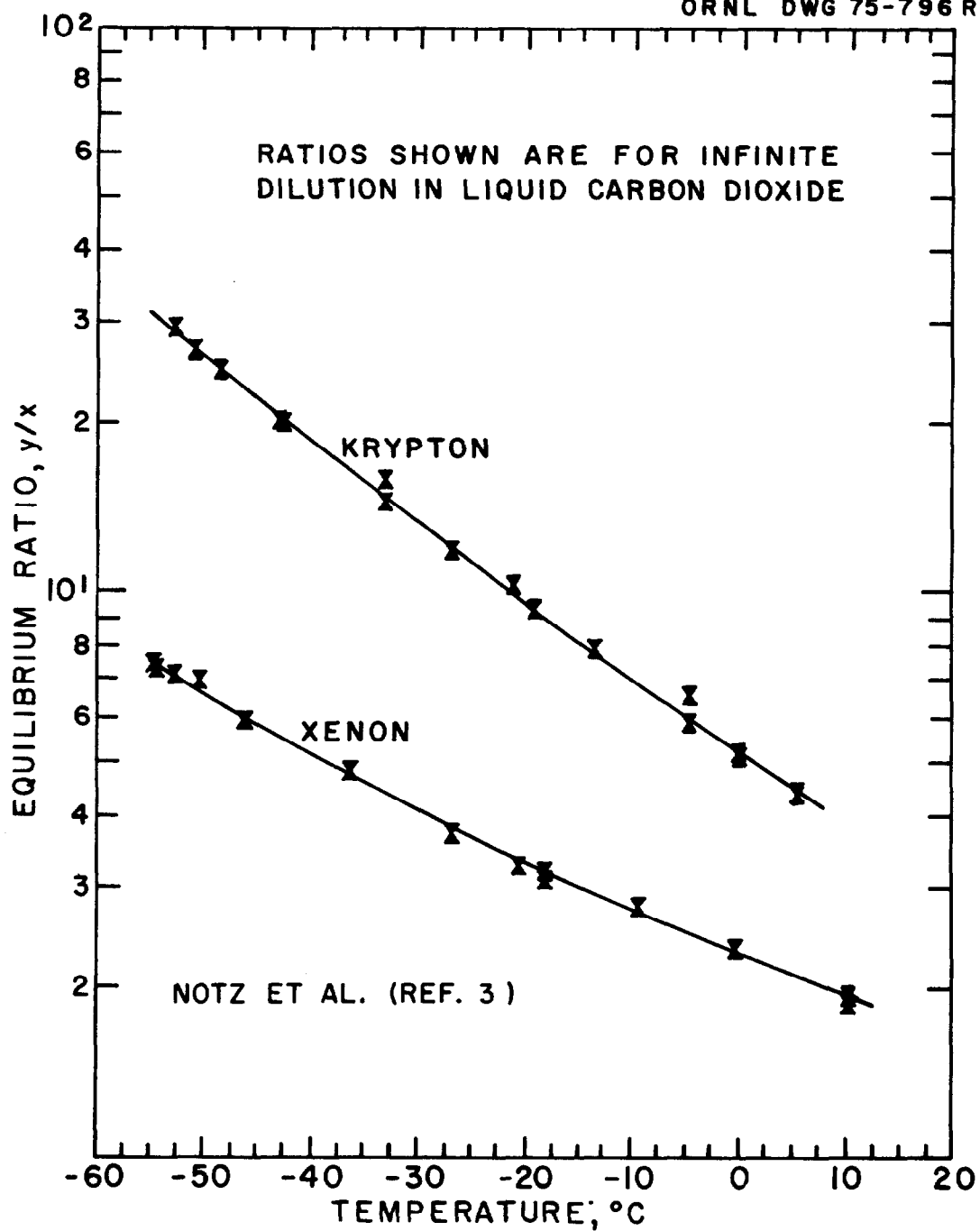


Fig. 4. Krypton and xenon equilibrium ratios as obtained by the computer model.

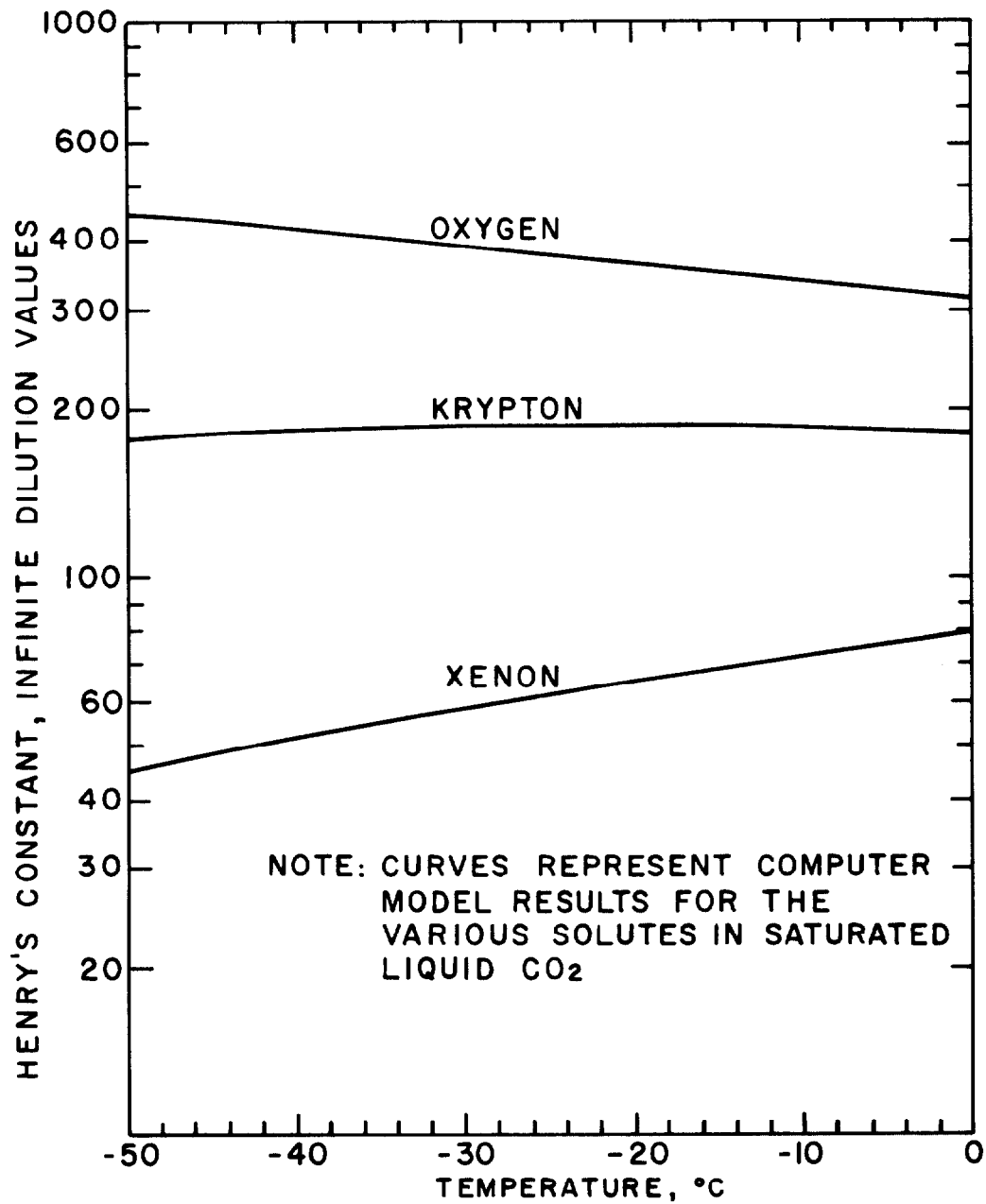


Fig. 5. Values of Henry's constant for selected solutes as obtained by the computer model.

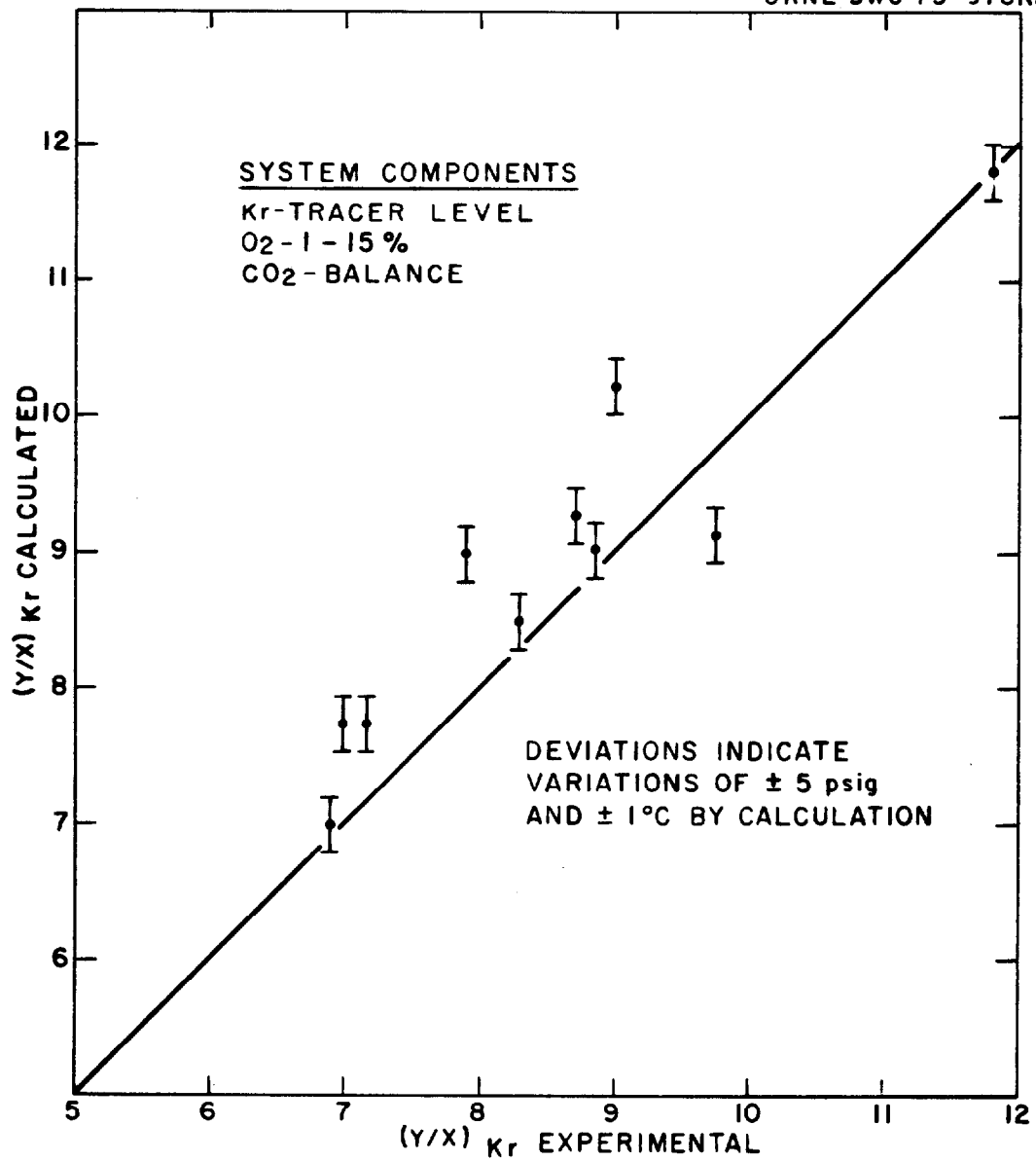


Fig. 6. Comparison of predicted and measured values of $(y/x)_{Kr}$ for the equilibrium experiments.

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the value of $(y/x)_{Kr}$ experimental was obtained directly. For each experimental value of P (total pressure) and T (system temperature at the bottom of the absorber), the computer model for the CO_2 - Kr - O_2 equilibrium provided a corresponding value of $(y/x)_{Kr}$ calculated. Additionally, the computer model provided a value of y_{O_2} at each P and T for comparison with the measured quantity.

Considering the range of concentrations involved (< 2 mole % O_2 in the liquid and tracer-level krypton), the agreement present in Fig. 6 is remarkably good and would tend to support the data of Notz et al.⁽³⁾ Thus, for the remaining experiments, the data of Notz et al. are assumed to be valid.

Mass Transfer Experiments

During the mass transfer experiments the EES-ODF was operated in total recycle with approximately 10% light gas (O_2) and tracer-level krypton. The simulated reprocessing off-gas stream was compressed to slightly more than the desired absorption pressure and routed to the bottom of the absorber column. In the absorber, the gas (flowing upward) was contacted with essentially pure liquid CO_2 into which both O_2 and krypton were absorbed as the liquid flowed down the packed section. The solute-laden liquid was then routed to the stripper column where the dissolved gases were desorbed and released into the stripper off-gas stream. The stripper and absorber off-gases were subsequently combined to form feed gas and recycled to the compressor. Liquid leaving the stripper was recycled to the top of the absorber packed section as a continuous flow of solute-free solvent.

For each of the mass transfer experiments, an operating condition was chosen and the entire flow system was allowed time for transients to subside before sampling and data acquisition. Tables 3 and 4 present a portion of the data taken during the mass transfer experiments, and include data for four experiments (viz., 232, 241, 254, and 538) which were made under pinched conditions that do not reflect the nature of the other mass transfer experiments. These four experiments simply offer a lower bound to operational mass transfer. Some of the values listed in Table 3 were obviously not obtained directly by experiment but, instead, were calculated from more fundamental measurements. The absorber pressure, average absorber temperature, absorber ΔP , and liquid rate are shown as measured. Feed gas rates were dependent on rotameter calibrations, while the O_2 content of the feed gas and overall krypton decontamination factors (DF's) were based on sampling and monitoring.

Data Analysis

During operations only the feed gas stream could be identified with respect to both flow rate (via rotameter) and composition (sampling and analysis). Off-gas streams from the absorber and from the stripper were sampled and analyzed for composition, but their flow rates were not known accurately since flowmeters for these streams were unreliable. Knowledge of the compositions (O_2 and krypton) for these streams, together with the flow rate of the feed gas stream, allows calculation of flow rates for the off-gas streams by assumption of either O_2 or krypton material balances in conjunction with overall stream balances.

Operational experience provides more confidence in the determination of the ⁸⁵Kr content; therefore, the assumption of a complete krypton balance was made,

Table 3. Summary of absorber conditions during mass transfer experiments

Experiment number	Absorber pressure (psig)	Feed gas rate (scfm) ^a	Feed gas oxygen (%)	Average absorber temp. (°C)	Absorber ΔP (in. H ₂ O/ft)	Liquid flow rate (gpm)	Overall krypton DF ^b
222	324	5.44	10.35	-20.0	0.364	0.551	357.
232	340	7.09	7.08	-17.4	0.516	0.551	5.
241	254	6.19	9.42	-28.2	0.255	0.485	7.
254	375	7.22	7.79	-12.2	0.619	0.485	3.
309	302	4.65	7.13	-20.1	0.413	0.623	256.
320	308	4.56	6.82	-20.1	0.510	0.720	14039.
330	308	4.57	7.83	-20.4	0.449	0.693	4161.
340	313	4.27	8.99	-20.5	0.473	0.693	7000.
348	310	4.55	9.19	-20.3	0.668	0.748	9687.
358	313	4.73	9.28	-20.8	0.467	0.665	619.
368	321	4.81	12.60	-20.9	0.516	0.623	7206.
378	337	4.99	11.70	-20.0	0.437	0.582	3214.
388	337	4.97	11.64	-20.0	0.449	0.582	3043.
406	384	5.87	20.06	-18.8	0.461	0.554	1215.
416	387	6.21	15.14	-18.3	0.394	0.485	1013.
426	347	5.74	11.93	-20.5	0.443	0.554	153.
436	345	5.39	10.75	-19.3	0.419	0.554	539.
451	325	4.77	11.34	-20.9	0.319	0.416	590.
461	336	4.40	10.47	-19.2	0.328	0.416	2602.
470	333	3.78	8.88	-18.7	0.316	0.416	3075.
480	317	5.23	10.83	-22.2	0.307	0.416	87.
490	323	6.33	8.62	-21.9	0.327	0.416	10.
498	323	3.73	8.45	-18.9	0.303	0.416	5157.
518	405	4.50	7.57	-12.6	0.376	0.416	839.
528	402	3.63	10.05	-11.7	0.376	0.416	4038.
538	409	6.38	7.80	-11.6	0.425	0.416	5.
548	396	5.16	5.93	-12.7	0.399	0.416	17.
558	391	4.67	6.79	-13.2	0.387	0.416	100.
568	407	4.23	6.24	-11.9	0.388	0.416	1100.
578	392	3.49	6.01	-12.17	0.376	0.416	2908.

^a scfm refers to real CO₂ gas at 70°F and 1 atm.^b DF = decontamination factor.

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Table 4. Mass transfer values

Experiment number	Overall DF	Column ^a DF	Krypton HTU (ft)	O ₂ balance factor	Absorption factor
222	357	227	0.561	0.93	1.29
232	5	5	1.329	0.94	0.81
241	7	7	0.700	0.94	0.90
254	3	3	3.220	0.97	0.72
309	256	219	0.355	0.94	1.15
320	14039	7757	0.383	0.84	1.43
330	4161	2750	0.339	1.06	1.32
340	7000	4139	0.385	1.02	1.43
348	9687	3866	0.348	1.02	1.45
358	619	471	0.380	1.02	1.23
368	7206	3350	0.374	1.10	1.41
378	3214	1927	0.405	1.02	1.42
388	3043	1887	0.400	0.97	1.40
406	1215	704	0.463	0.99	1.34
416	1013	621	0.464	1.05	1.30
426	153	115	0.506	0.97	1.19
436	539	343	0.493	0.99	1.33
451	590	354	0.430	0.93	1.27
461	2602	1267	0.418	0.94	1.42
470	3075	1358	0.482	0.95	1.55
480	87	72	0.345	0.99	1.07
490	10	10	0.588	0.92	0.92
498	5157	2119	0.441	1.08	1.58
518	839	642	0.400	0.98	1.26
528	4038	2455	0.378	0.92	1.40
538	5	6	1.720	0.98	0.87
548	17	18	0.816	0.99	1.02
558	100	96	0.479	0.96	1.13
568	1100	830	0.448	0.98	1.32
578	2908	1543	0.419	0.94	1.41

^a Column DF's are calculated values which pertain to conditions at the top and bottom of the packing itself.

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and the inaccuracies involved in flow rate, O_2 content, and krypton content have been combined into the oxygen balance factor noted in Table 4.

The overall krypton DF as presented in Table 3 is calculated from the krypton present in the feed gas and absorber off-gas streams as follows:

$$\text{Overall DF} = \frac{\text{Amount of Kr in feed gas}}{\text{Amount of Kr in absorber off-gas}} \quad (2)$$

Calculations of HTU's for krypton are based on the following simple and classical equations:(8)

$$\text{HTU} = Z/\text{NTU}, \quad (3)$$

$$\text{NTU} = \frac{y_o - y_i}{(y^* - y)_{\text{lm}}}, \quad (4)$$

$$(y^* - y)_{\text{lm}} = \frac{(y_o^* - y_o) - (y_i^* - y_i)}{\ln \frac{y_o^* - y_o}{y_i^* - y_i}}, \quad (5)$$

where

HTU = height of transfer unit, ft,

Z = column packing height, ft,

NTU = number of transfer units,

y_i = inlet gas composition,

y_o = outlet gas composition.

Asterisked quantities (e.g., y_i^*) indicate phase compositions that are in equilibrium with corresponding compositions in the adjacent phase. All compositions refer to krypton; $Z = 8.24$ ft and $y_o^* = 0$. Values of HTU calculated by using Eq. (3) are presented in Table 4. Figure 7 illustrates the variation of the packing HTU with column DF. Figure 8 shows the variation of column DF with absorption factor.

Discussion

As necessary for clarity, certain details have been included with the experimental and analytical procedures already presented. A more complete discussion of the present work is presented in Reference 9. Earlier campaigns and reports concerning the EES-ODF have noted the experimental nature of the facility. The presentation of details indicate clearly one aspect of this facility. The facility, by design, is intended to provide development data as opposed to demonstration-type information. Development data collected relate specifically to krypton absorption by liquid CO_2 . Subsequent work will be concerned with other operations of importance in the KALC process, such as fractionation of lighter gases that are coabsorbed with krypton or complete stripping of all

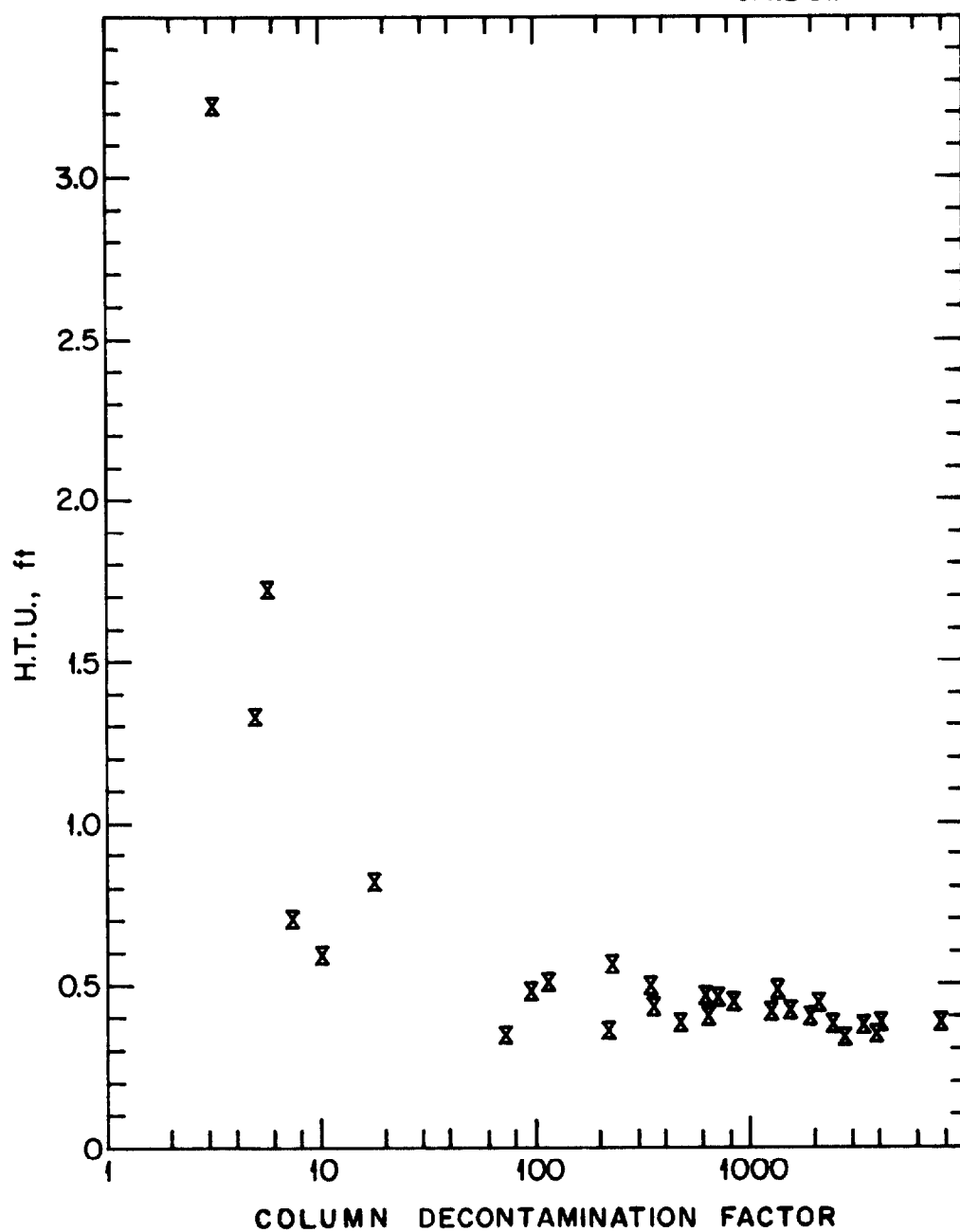


Fig. 7. HTU values for mass transfer experiments.

ORNL DWG 75-5352 R2

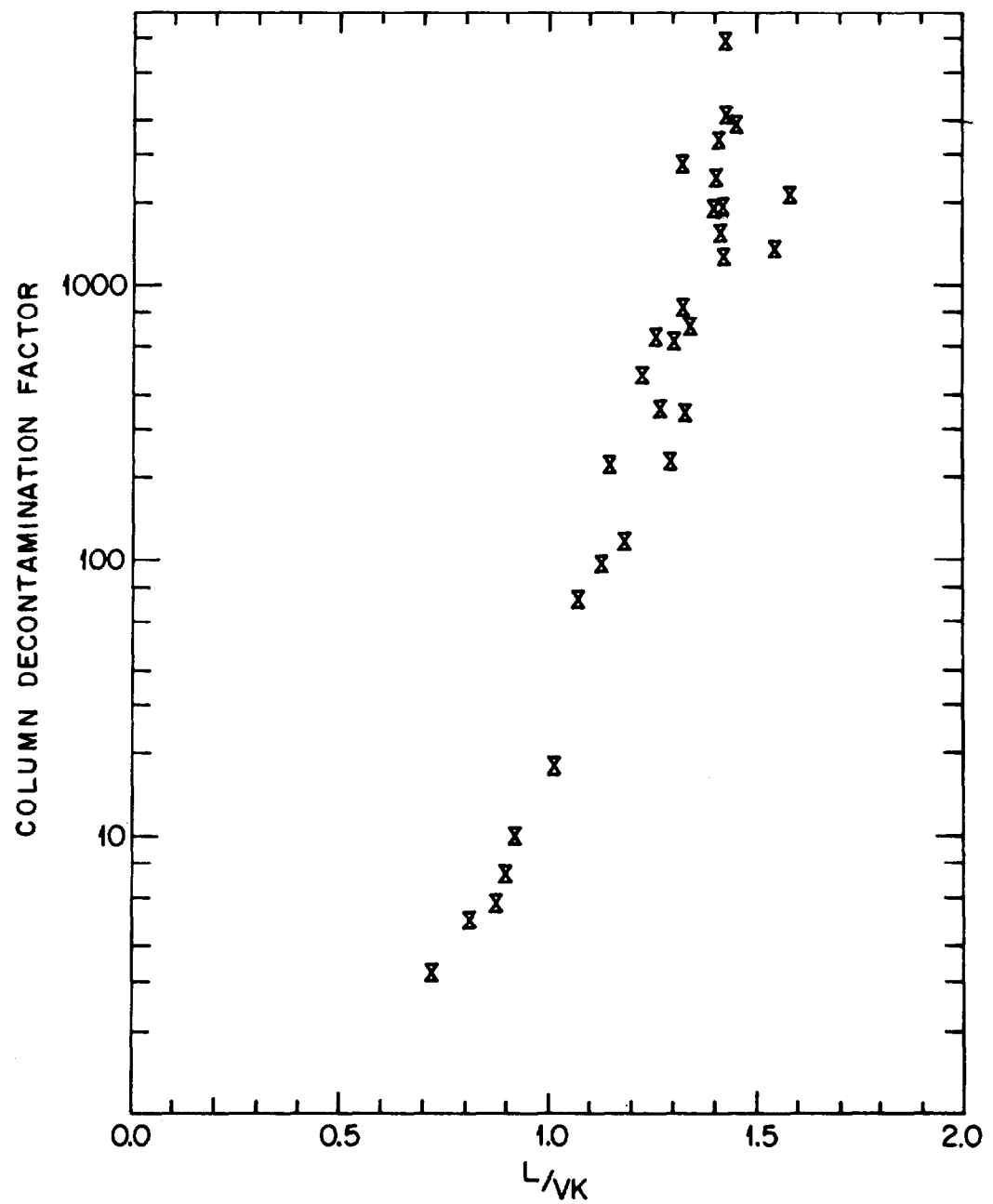


Fig. 8. Decontamination factors vs absorption factors.

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dissolved light gases. Each of these operations is important in the total development of the KALC process, but the EES-ODF is not designed to study all operations simultaneously. The facility is not a prototype KALC system. Rather, it represents an engineering-scale system designed to study individual operations of the KALC process under experimental conditions as closely similar to those expected in an overall process as possible.

Many features of the EES-ODF will undoubtedly have counterparts in a conceptual or subsequent design of the KALC system; however, such features will require technical review for operability, compatibility, and desirability before scale-up to the commercial or semicommercial system can occur.

The curve shown in Fig. 2 is of the form typically presented⁽¹⁰⁾ as the "generalized" flooding curve except that the usual parameters, a_p/ϵ^3 , in the ordinate grouping for the particular packing characteristics have been omitted. (Generally, a_p is the total area of packing (ft²/ft³ bed), and ϵ is the void fraction in dry packing.) Moreover, the curve in Fig. 2 only resembles the generalized curve and does not correspond exactly in shape. At any value of the abscissa grouping, the ratio a_p/ϵ^3 (i.e., the packing factor) can be evaluated by calculating the ratio of the generalized curve ordinate grouping to that of Fig. 2. For example, at a value of the abscissa grouping of unity (near the center of both flooding curves), the packing factor is calculated to be 215 by this method. Hence, in the instance described, the packing of Fig. 2 may be compared to other types as follows:

<u>Packing type</u>	<u>a_p/ϵ^3</u>	<u>Relative factor</u>
1/2-in. ceramic Raschig rings	428	1.99
5/8-in. polypropylene Pall rings	158	0.73
1/2-in. ceramic Berl saddles	596	2.77
1/2-in. ceramic Intalox saddles	400	1.86
Goodloe wire mesh packing	215	1.00

The relative factors presented above do not necessarily indicate a packing quality or utility higher or lower than the packing used. Two important performance considerations here are throughput (or capacity) and HTU.

Figure 2 presents evidence that the flooding characteristics of the packing for the 1-1/2-in.- and 3-in.-diam columns are essentially identical for the conditions investigated. Whether identical results will also be obtained in larger-diameter columns is not known. The effect of packing density has not really been determined for the wire mesh packing investigated.

It should be noted that in the event that diameter greatly influences the flooding (and therefore the capacity) in large columns, the use of other "dumped" packings would not circumvent this problem. In fact, the relative size of dumped packing to column diameter may be more difficult to handle for scale-up purposes than considerations of the density of mesh packing.

From the standpoint of capacity and within the available time for testing, it appears likely that the wire mesh will provide a reasonable basis for scale-up without undue compromise in mass transfer performance. Also, this material will probably be at least comparable, with regard to capacity, to other commercially available packings.

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The question of mass transfer performance is another important consideration when selecting a packing material. The present work concerns only absorption in the 1-1/2-in. EES-ODF column. Figure 7 shows that for reasonable values of operational parameters a value of 0.4 to 0.5 ft for HTU results. A number of considerations relating to the accuracy of the calculational procedures will be discussed later. Of question here is whether the HTU value will vary appreciably with column diameter. Obviously, the question cannot be answered from the present absorption experiments alone.

Most of the important considerations in equilibrium operations have been discussed previously. At the time the experiments were performed, valid questions existed as to (1) the importance of the equilibrium data accuracy, and (2) the effect of uncertainties in the equilibrium ratios (y/x). Certainly, the data of Notz et al. do exhibit an internal consistency over a relatively large range of temperatures, and all of their data are reported at essentially infinite dilution. Correlation techniques were used by Mobley to test the apparent consistency with other solutes in liquid CO_2 . The net result of the equilibrium operations, together with the finding of Mobley, is that, while the data of Notz et al.³ are definitely more nearly accurate, a margin of uncertainty regarding absolute accuracy remains.

Just how important it is that the Kr-CO_2 equilibrium values are known to within a given range, say $\pm 10\%$, is not clear. Based on HTU values calculated with Eq. (3), a qualitative relation exists between HTU and K as follows:

$$\text{HTU}_2 = \text{HTU}_1 \left[\frac{K_2}{K_1} \right]^{-3} \quad (6)$$

Consequently, a 10% variation in K (i.e., $\pm 5\%$) would result in a $\pm 15\%$ uncertainty in HTU. Such an uncertainty in HTU would not be unacceptable per se; however, the true range of uncertainty would undoubtedly be larger since other factors are known to contribute.

Figure 6 indicates a slightly lower experimental value of $(y/x)_{\text{Kr}}$ than one would predict using the data of Notz et al. Mobley's findings via correlations also indicate a slightly lower value and thus tend to fall more in line with other solute behavior in liquid CO_2 . Both the equilibrium operations considered here and elements of the correlation work exhibit uncertainties, so that it cannot be stated absolutely that the data of Notz et al. are in error. Finally, although the equilibrium experiments were tedious and time-consuming, perhaps more confidence could be placed in the results if additional experiments had been conducted. At the present time, however, there appears to be no compelling reason why the data of Notz et al. should not be accepted.

During the present mass transfer experiments, the independent variable of primary importance was the absorption column liquid-to-vapor flow ratio (L/V). Ranges for this and other important variables are summarized as follows:

<u>Variable</u>	<u>Range</u>
Pressure, psig	254 to 409
Temperature, °C	-28.2 to -11.6
Feed O_2 concentration, vol %	5.93 to 20.06
Liquid-to-vapor ratio	
Overall values	4.94 to 12.82
Column only	5.04 to 12.88

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It should be recognized that a 1:1 correspondence does not exist for the above variables over their ranges. That is, the experiment with the highest pressure is not necessarily the experiment with the highest L/V , etc. However, the variables are not totally independent, and a careful review of all variables presented throughout this report is necessary for an appreciation of the nature of the absorption process.

An important experimental observation is that variables do behave relative to one another as would be expected based on thermodynamic and chemical engineering principles. In short, no surprises were found. Of equal importance was the considerable operational experience gained, which will be of use in subsequent campaigns and for scale-up design analyses. In some ways, the study of absorption may be the least difficult of the studies required (viz., absorption, fractionation, and stripping). However, there are certain similarities among the three studies, and the discussion presented in this report regarding absorption should be applied to future plans for fractionation and stripping experiments.

The few results that indicate appreciably higher values of HTU than 0.4 ft (see Fig. 7) were obtained in essentially pinched experiments, where the HTU equation is erroneously attributing all the mass transfer to the entire packing length instead of to the shorter, effective length. The result is a higher apparent HTU value, and this phenomenon is not unexpected. The fact that Fig. 8 shows a rather sharp increase in DF as the value of the "absorption factor," L/VK , exceeds unity is indicative of (1) more than just a "few" stages in the absorber, and (2) the "correct" choice of experimental Kr-CO₂ equilibrium data. If only a few stages were present, it would be expected that DF would not increase as rapidly with L/VK . If the data of Beaujean et al.² were correct (or if the data of Notz et al. were grossly in error), the "inflection" of the DF curve of Fig. 8 would not necessarily be at $L/VK = 1$. Of course, the value of L/V used in L/VK could be in error; nevertheless, it is doubtful that the general error associated with L/V would exactly compensate for a corresponding uncertainty in K . Further, since DF is essentially a measured quantity, the ordinate of Fig. 8 can be expected to be indicative of the true situation as far as curve shape is concerned.

Conclusions

The present work has provided a wealth of operating experience on which subsequent operations can realistically be based. Sampling and analytical techniques appear to be valid and provide a relatively quantitative measurement of composition. However, the absolute accuracy of composition measurements can be evaluated only with additional experimentation.

Flooding performance of the wire mesh packing is reasonably well correlated for the conditions and equipment studied. The krypton equilibrium data of Notz et al.⁽³⁾ appear to be sufficiently accurate for experimental purposes of the EES-ODF. For process decontamination factors on the order of 1000, a value of 0.5 ft for the krypton absorption HTU seems realistic and, within the range of the experiments conducted, does not vary for reasonable absorption conditions.

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EXPERIMENTAL DETERMINATION OF REACTION RATES OF WATER - HYDROGEN EXCHANGE OF TRITIUM WITH HYDROPHOBIC CATALYSTS

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Abstract

This study was undertaken to obtain data needed for further development of a process for the enrichment and removal of tritium from the water associated with light-water reactors, fuel-reprocessing plants, and tritium-handling laboratories. The approach is based on the use of antiwetting, hydrophobic catalysts which permit the chemical exchange reactions between liquid water and gaseous hydrogen in direct contact, thus eliminating problems of catalyst deactivation and the complexity of reactor design normally associated with current catalytic-detrutiation techniques involving gas-phase catalysis. An apparatus and procedure were developed for measuring reaction rates of water-hydrogen chemical exchange with hydrophobic catalysts. Preliminary economic evaluations of the process were made as it might apply to the AGNS fuel reprocessing plant.

I. Introduction

There has been a rapid increase in both the size and number of nuclear reactors used in the generation of electrical energy. These reactors produce a large quantity of radioactivity primarily resulting from the fission process. The release of radioactivity from a light water reactor is very small, and most of the fission products, including tritium, are transported to the fuel reprocessing plants in the spent fuel elements. Here the fission products are separated from the fuel which is recycled, and nearly all these fission products, with the exception of krypton and tritium, are concentrated and stored. Current practice is to release all the tritium to the environment as HTO either via a stack to the atmosphere or by injecting it into surface or deep well waters. The existing ERDA fuel reprocessing plants discharge their tritium in a liquid waste stream to surface waters. The AGNS plant at Barnwell, N.C., is designed to discharge the HTO through a stack to the atmosphere. The NFS plant, now undergoing modifications to increase its capacity, discharges 90% of its tritium to surface waters and 10% through stack effluents. These discharges represent the largest release point for radioactive material in the entire fuel cycle.

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Because of the expanding nuclear power industry and the increased emphasis on minimizing release of radioactive materials to the environment, there is an increasing need for the development of safe handling and disposal methods for the radioisotopes being produced. With the exception of tritium, all the radioisotopes produced in the operation of a light-water reactor are amenable to some form of chemical or physical separation process for removal from the effluent streams. Tritium, however, is generally encountered in the oxide form and therefore follows the natural water streams. The detritiation of these aqueous wastes requires isotopic separation processes.

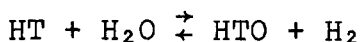
The purpose of this study is to develop a tritium separation and concentration process based on a H_2/H_2O catalytic exchange technique which can be used to detritiate contaminated water from light-water reactors, fuel-reprocessing plants, and tritium-handling laboratory facilities.

II. Catalytic Exchange Separation of Hydrogen Isotopes

Work in progress is directed toward development of an improved version of the basic HT/H_2O catalytic exchange process and demonstration of the separation of tritium for the particular concentrations and types of low-level aqueous wastes (LLAW) obtained from light-water reactors and fuel-reprocessing plants. The process will also apply to the removal of tritium from heavy water (D_2O) used as the moderator and coolant in several research and all U.S. government production reactors.

The improved approach to HT/H_2O catalytic exchange is based on the use of antiwetting hydrophobic catalysts which permit the chemical exchange reactions between liquid water and gaseous hydrogen in direct contact, thus eliminating problems of catalyst deactivation and the complexity of reactor design normally associated with current catalytic exchange techniques ⁽¹⁻³⁾ involving gas-phase catalysis. Use of hydrophobic catalysts was first reported ⁽⁴⁾ in relation to studies directed toward an improved heavy-water process. The catalyst consists of platinum on an alumina substrate with a coating of semipermeable, water-repellent material such as silicone or Teflon.

The highest isotopic separation factors for HT/H_2O exchange are obtained at low temperatures because of the nature of the chemical equilibrium,



with a value of the isotopic separation factor of about 6 at 25°C. The processes involving steam-hydrogen reactions in the vapor state require higher temperatures to prevent water condensation and are faced with the resulting lower isotopic separation factors.

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The hydrophobic low-temperature mixed-phase system potentially has many advantages over the gas-phase system; for example, higher isotopic separation factor, lower energy consumption, higher throughput rate, and simpler equipment.

There are two major alternative applications of the HT/H₂O catalytic exchange process to detritiation of LLAW. The first alternative is to apply the process to the total waste stream and deplete the tritium to a degree that the resulting detritiated waste stream may be dispersed to the environment. This alternative has been referred to by Ribnikar and Pupezin⁽⁵⁾ as the stripping scheme. The second alternative application would produce a similar enriched tritium stream, but the water is detritiated to a lesser degree and returned to the reactor (or plant), thus maintaining a desired steady tritium concentration in accord with applicable regulations for in-plant exposure of operating personnel. Ribnikar and Pupezin⁽⁵⁾ have called this alternative the recycling scheme. Of course, a wide spectrum of options exists within either scheme when a design basis for the detritiation system is selected. For example, regulatory factors and in-plant parameters such as LLAW throughput quantity and tritium concentration levels could affect the size of the system and the necessary degree of separation and enrichment of the tritium.

The throughput required for removal of tritium from LLAW could vary over a wide range depending on the application. Likewise, the degree of separation and recovery required could vary considerably. For example, the internal flow of water in a PWR cooling-water recycling detritiation application could be on the order of 10-50 liters/hr with an overall separation factor requirement of 100 to 1000. In comparison, application of the stripping scheme to the flow of LLAW from a fuel reprocessing plant could require a throughput of 500-2500 liters/hr with an overall separation requirement of 10¹¹ to 10¹³. Since the costs associated with detritiation of water increase with increased throughput and also increase with the increased overall separation factor, the application of the stripping scheme to the fuel reprocessing plant would be the most costly, as both throughput and separation requirements are a maximum for the fuel reprocessing LLAW stripping application.

The fuel reprocessing plant application of the waste water detritiation process was chosen for economic evaluation on the basis of being the most stringent, and most costly, application in the fuel cycle.

Preliminary Economics

A preliminary economic evaluation was made of the HT/H₂O catalytic exchange detritiation stripping process as it might apply to the Allied-Gulf Nuclear Services (AGNS), Barnwell, S.C., 5-metric ton/day nuclear-fuel-reprocessing plant. A schematic of the stripping process is given in Figure 1. This processing scheme would

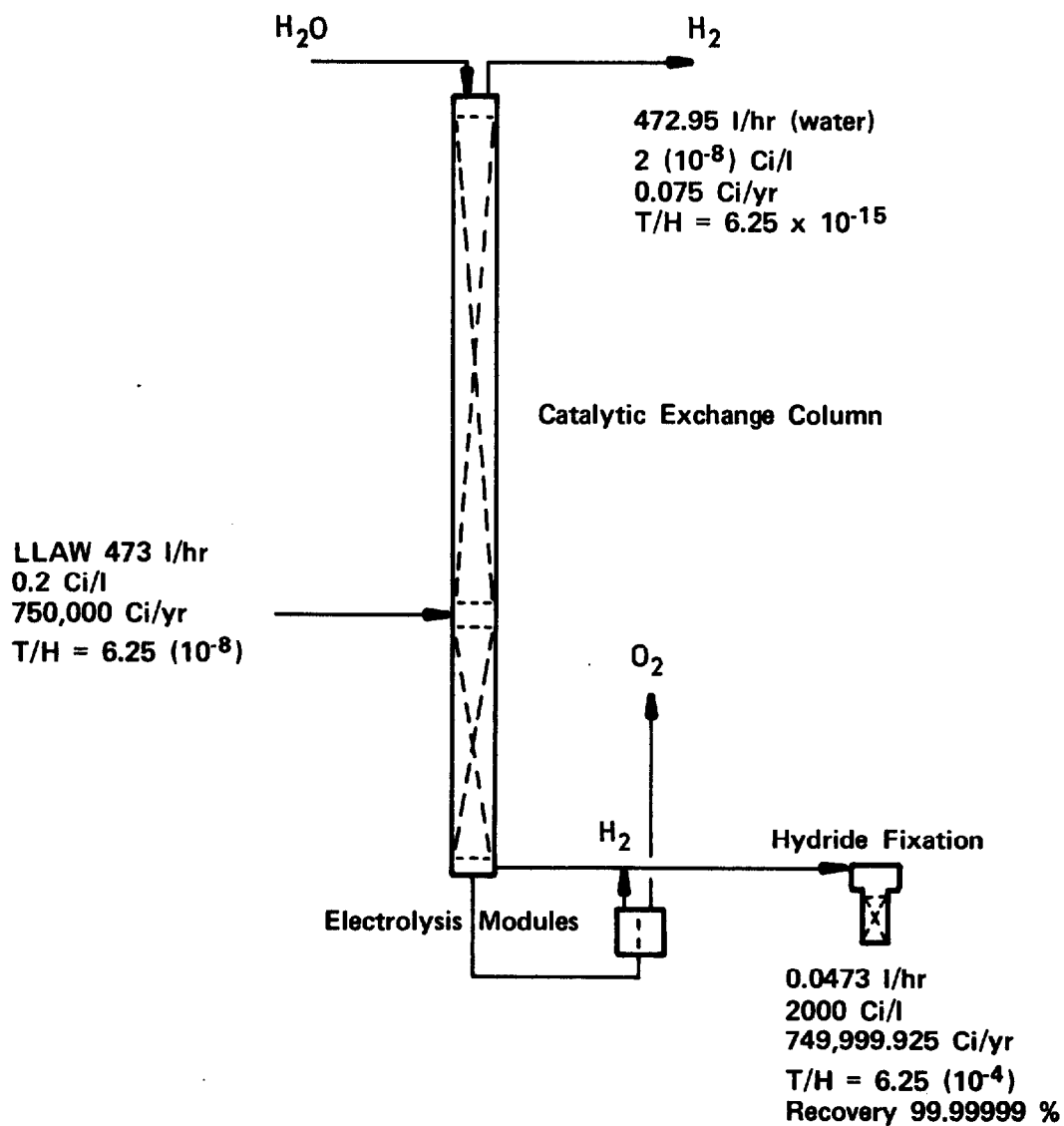


FIGURE 1 AGNS LLAW detritiation.

detritiate approximately 500 liters/hr of LLAW containing 0.2 Ci/liter of tritium to an extremely stringent degree. Of the tritium contained in the aqueous waste stream (750,000 Ci/yr), 749,999.925 Ci/yr would be concentrated in a quantity of water which would be only 47.3 cm³/hr, or the equivalent quantity of gaseous hydrogen isotopic mixture, 5900 cm³/hr of gas. The remainder of the 500 liters/hr feed stream would be detritiated to such a degree that it would be below the newly proposed EPA drinking water standard of 20,000 pCi/liter.⁽⁶⁾

Operation cost estimates are given in Table 1. The operating cost of \$1,800,000 per year may be compared to the projected cost of biological damage due to released tritium from a 5 metric ton/day reprocessing plant. The recent tentative assignment of \$1000 per total-body man-rem by the NRC and the whole body dose for tritium from a 5 metric ton/day fuel-reprocessing plant of 3,700 man-rem per year, as projected by the EPA, were used to obtain a cost for biological damage due to release of tritium of \$3,700,000 per year. Thus the estimated operating cost of \$1,800,000 per year is well below the cost-benefit balance point. Presumably, applications of the process in a recycling scheme or other less stringent applications than chosen for the above analysis would be even more economically favorable.

On the basis of the above preliminary economic evaluation, the HT/H₂O catalytic exchange detritiation process is judged worthy of further research and development effort.

Experimental

A bench-scale experimental apparatus was built for operation in a controlled glovebox under recirculating helium atmosphere. Figure 2 is a schematic of the experimental apparatus.

The experimental system is comprised of a low-temperature (20-70°C) reactor (3.8 cm i.d. x 28 cm), a high temperature (100-500°C) reactor (3.8 cm i.d. x 28 cm), support equipment, and analytical instruments. The low-temperature reactor packed with hydrophobic platinum-coated catalyst (0.48 cm diam.) was designed for a liquid gas countercurrent flow, and tritium is enriched in the liquid water (i.e., H₂O(l) + HT → HTO(l) + H₂). The high-temperature reactor with regular nonhydrophobic platinum-coated catalyst (0.32 cm diam. x 0.32 cm) was built for a gas-gas cocurrent flow, and the tritium was depleted from the water vapor (i.e., H₂O(g) + HT → HTO(g) + H₂). Hence, with these two reactors combined in a system consisting of an evaporator, condenser, phase separator, pumps, etc., a complete closed-loop experimental apparatus involving gas-phase and liquid-phase tritium exchange reactions is obtained. This apparatus is capable of continuous recycling of the enriched and depleted water and hydrogen streams. Operating parameters, such as flow rate and temperature, may be adjusted and steady state conditions may be obtained. Reaction rates are then measured.

TABLE 1 Operation cost estimate AGNS LLAW detritiation.

Detritiated Water - 3.75 (10 ⁶) liter/yr				Unit Investment:	
750,000 Ci/yr @ 0.2 Ci/liter				On Site	\$ 3,817,000
On Stream 330 days/yr				Off Site	<u>1,336,000</u>
Recovered Tritium 749,999.925 Ci/yr					
375 liter/yr @ 2000 Ci/liter				Total	\$ 5,153,000
Item	Quantity, yr	Cost/unit	Cost/yr	Cost/Ci	
Variable Costs:					
Cooling H ₂ O	60,300 kgal	\$ 0.02	\$ 1,000		
Electricity	4.17 (10 ⁷) kWhr	0.025	1,043,000		
Catalyst	950 lb	20.00	<u>19,000</u>		
Total Variable Costs			\$1,063,000		\$ 1.417
Fixed Costs:					
Direct Labor 8,760 man hr @ \$6.00			\$ 53,000		
Supervision @ 20% DL			10,000		
Maintenance @ 4% PI			153,000		
Supplies @ 10% Maintenance			15,000		
Payroll Burden @ 30% DL			19,000		
Taxes and Insurance @ 3% PI			114,000		
Depreciation 10% Straight Line			<u>382,000</u>		
Total Fixed Costs			\$ 746,000		\$ 0.995
Total Operating Costs			\$1,809,000		\$ 2.412

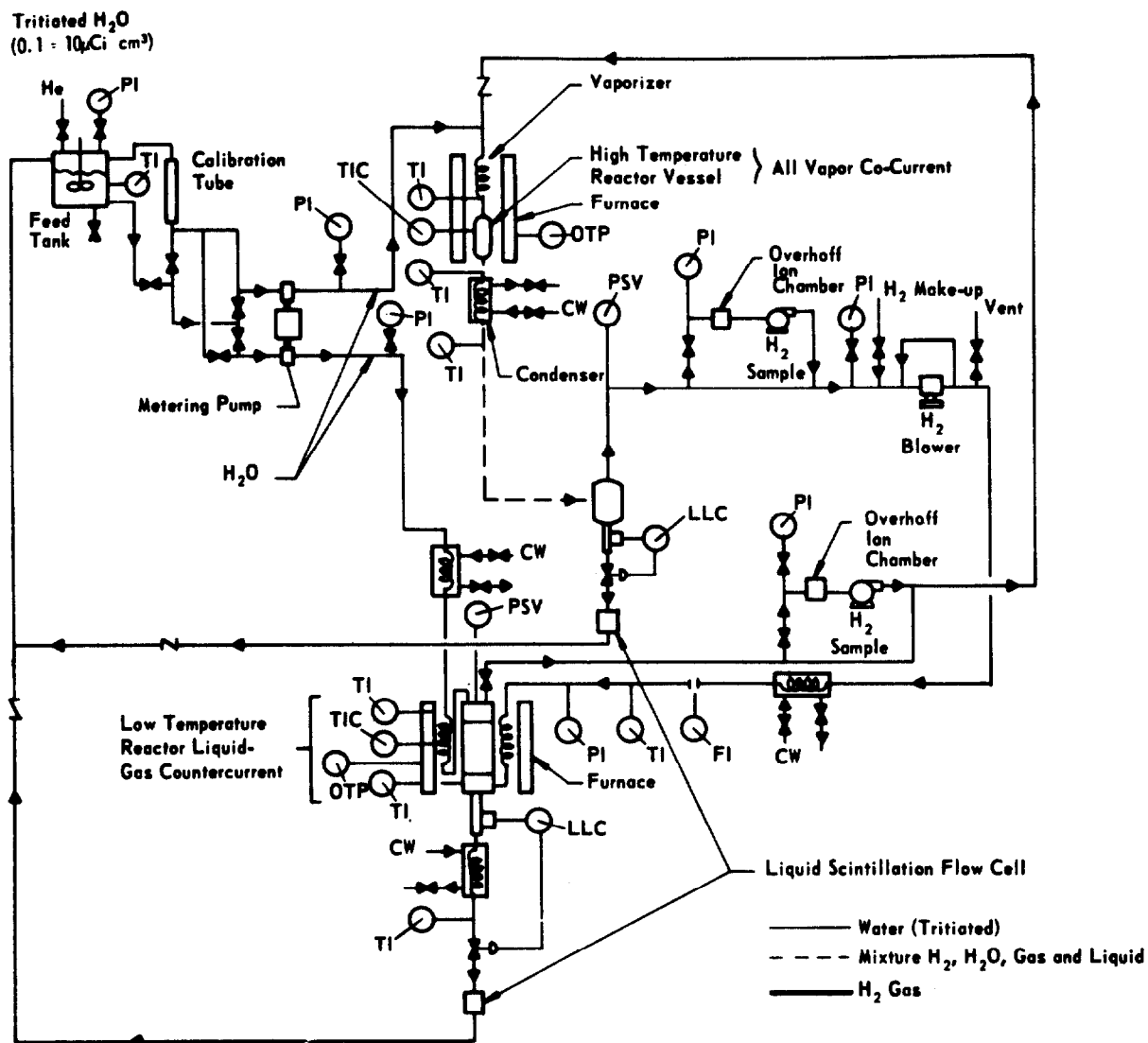


FIGURE 2 Experimental system for measuring reaction rates of water-hydrogen chemical exchange.

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This apparatus is being used for catalyst evaluation tests; the first catalyst to be evaluated is an Engelhard Minerals and Chemicals Company hydrophobic catalyst consisting of platinum on an alumina substrate with a semipermeable coating of a proprietary water-repellent material.

Experimental Results

The height of one equilibrium stage has been calculated from the data to be 18 ft. Since the preliminary economic evaluation (Table 1) was conducted with an assumed height of 20 ft, the 18-ft height calculated from the data would enhance the economic evaluation. The hydrophobic catalyst, therefore, appears to be propagating the liquid-gas chemical exchange effectively.

Discussion

The experimentation is continuing in order to generate data at different parameters of flow rate, temperature, and tritium concentration. The development of the mechanism of the exchange, as well as the optimum operational parameters, is to be completed. This information will be used to scale up to a pilot-plant exchange system.

Conclusion

Kinetic and thermodynamic performance data will be obtained and evaluated not only on the Engelhard catalyst, but also on a catalyst developed by Atomic Energy of Canada, Ltd., who have an interest in the catalytic exchange detritiation process for their heavy-water reactor program. In 1975, an agreement was initiated between ERDA and AECL for a cooperative program to share information concerning the catalytic exchange detritiation process. Work on the process will continue.

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DISCUSSION

R. A. BROWN: What will be the impact of the many contaminants in fuel reprocessing plant aqueous streams on performance?

BIXEL: We have considered it and it's probably going to be necessary to have pure water going into the catalytic exchange column. The water will probably have to be demineralized.

R.A. BROWN: That might be an important consideration in your design expansion.

BIXEL: This is something we will investigate in our experiments. I hope we will be able to determine the effect of trace elements.

RICHARDSON: I would like to make a brief comment on the drinking water standard that you referred to. That standard is not any longer proposed. It is effective July of this year, but I think we should put it in perspective. The standard applies to drinking water at the tap. I think it is fairly unlikely that people would be drinking effluents from your system.

BIXEL: I agree.

YARBRO: I was a little concerned about your presentation of cost benefits. Correct me if I am wrong, but I think the thousand dollar per man-rem you quoted as an NRC number applies to a 50 mile radius. The 3,000 plus man-rem EPA number, I believe, is a long-term worldwide integrated dose. I think you are multiplying apples times oranges and I believe this calculation is misleading.

BIXEL: It is my understanding that the thousand dollars per man-rem applies to world wide exposures.

YARBRO: I believe that it is specifically stated to be for a 50 mile radius.

BIXEL: I don't see the logic to applying it only to a 50 mile radius.

SKOLRUD: Have you investigated or determined the performance of this catalyst in pure gas phase applications rather than just for an aqueous gas mixture?

BIXEL: It appears that other catalysts are better in the gas phase. Our experimental system has two reactors, one, a gas phase reactor and the other, a countercurrent two-phase reactor, and we use different catalysts. The gas phase catalyst is better for gas phase exchange. We haven't tried the hydrophobic catalyst in the gas phase.

SKOLRUD: You stated that you were going to investigate the effect of contaminants in the aqueous phase stream in this application. What contaminants do you anticipate will be included in the future tests of catalytic exchange?

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BIXEL: We would have to get some information from the fuel reprocessing people on what they expect in their water streams.

VAN BRUNT: Do you foresee any adverse interaction of deuterium on your process?

BIXEL: Yes. That is a complicating factor in the isotopic separation. Of course, deuterium is there to the extent of 150 parts per million. This is a much higher level than tritium. In the process of concentrating tritium, deuterium is also concentrated. Separating tritium from deuterium has a lower separation factor of about 1.5.

COLLINS: I would like to comment on the use of a thousand dollars per man-rem. The statement is right, it is for a 50-mile radius. I think your use of the thousand dollar figure in that sense is not correct.

BIXEL: Apparently I stand corrected.

DEMPSEY: The other alternatives are also very costly. I would just like to remind the audience that in the preprint envelope, we included a copy of a portion of the TAD document which covers this point and some others that will be discussed this afternoon.

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SEPARATION OF KRYPTON FROM CARBON DIOXIDE AND OXYGEN WITH MOLECULAR SIEVES*

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Abstract

Molecular sieves were investigated to separate 1% mixtures of krypton in gas streams containing 90+% CO₂ and a few percent O₂. Such a system will be required to concentrate the krypton gas between radioactive off-gas cleanup systems such as KALC⁽¹⁾ (Krypton Absorption in Liquid Carbon Dioxide) and any krypton gas bottling station. Linde 5A molecular sieve was found to be capable of selectively removing the CO₂ from the gas stream while partially separating the oxygen from the krypton, i.e., effecting a three-component gas separation. This use of molecular sieves differs from standard practice in two respects: (1) bulk removal of the gas (>90%) is accomplished rather than the normal practice of removing trace impurities and (2) two separations, CO₂ from other gases and krypton from oxygen, occur simultaneously in a single bed. The use of molecular sieves for separating krypton and carbon dioxide is superior to alternatives such as CO₂ freezeout and chemical traps when there are only moderate gas flows and there is a need for very high reliability and ease of maintenance.

I. Introduction

The general approach in reprocessing HTGR nuclear fuels containing large amounts of carbon is to burn the fuel to release the fissile and fertile material. The burning process produces a CO₂-rich gas which contains all other gases in the fuel, including radioactive krypton. Since radioactive krypton cannot be released to the atmosphere, it must be removed. A process called KALC (Krypton Absorption in Liquid Carbon Dioxide)⁽¹⁾ has been developed to remove this radioactive krypton from the off-gas stream; however, KALC does not produce a pure product stream of krypton gas. (This is also true of several alternative processes.) Although 99+% of the krypton is removed from the off-gas by KALC and the isolated krypton may be concentrated by a factor of a 1000, the final krypton product stream contains less than 2% krypton, 0 to 5% O₂, 0 to 5% xenon, with the remainder being CO₂.

It is desirable for safety⁽²⁾ and economic reasons to concentrate this krypton product further by removal of all CO₂ and most of the O₂ before bottling the krypton. The CO₂ and O₂ removed in this step, if contaminated with radioactive krypton, can be recycled back to the front end of the primary krypton removal system. The gas flows in this secondary system are so small, as compared with the primary system, that complete recycle of CO₂ and O₂ will not

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significantly affect the primary system. Evaluation of many alternatives, including chemical adsorbents and CO₂ freezeout, indicate that molecular sieves would be preferred on the bases of reliability, performance, and safety. Initially, the removal of only CO₂ was planned; however, experiments also showed the feasibility of removing most of the oxygen. Hence, it was decided to take advantage of this additional capability.

II. Basic Process

The process for separating krypton from O₂ and CO₂ is based on the gas adsorption characteristics of molecular sieves. Molecular sieves are alumina-silicate crystals which have the ability to adsorb certain gases, such as CO₂, up to 20% of their own weight. By using molecular sieves in a manner similar to a frontal analysis gas chromatograph⁽³⁾, separation of a mixture of krypton, O₂, and CO₂ into relatively pure components in a single column is possible.

Column Behavior

If a gas mixture of krypton, O₂, and CO₂ flows through a bed of 5A molecular sieve near atmospheric pressure at 0°C, both CO₂ and krypton will be adsorbed. Carbon dioxide is, however, more strongly adsorbed than krypton and thus will displace krypton gas from the bed. In examining a long molecular sieve bed supplied with a feed gas of O₂, krypton, and CO₂, one observes that the zone of the molecular sieve bed nearest the feed point is saturated with CO₂ while the gas phase contains the feed gas. At the end of this zone, there is a transition region where CO₂ is being adsorbed onto the bed and krypton is being displaced from the bed into the gas phase. Beyond this first transition region is a zone where adsorbed krypton is held by the bed and only oxygen and krypton exist in the gas phase. At the end of this zone lies a second transition region where krypton is being adsorbed onto the bed. Beyond the latter region are found only oxygen and a molecular sieve bed which has very little gas adsorbed on it.

If the gas mixture is continuously fed to the bed and the gas exiting from the bed is analyzed, a bubble of oxygen is first observed, followed and pushed out successively by a bubble of krypton containing some oxygen and by the feed gas. At the end of this process, the bed is saturated with adsorbed CO₂. Heat is generated during the process, therefore, provisions for heat dissipation must be included since the bed must be kept at constant temperature to ensure good separations.

Plant Design

Two columns filled with molecular sieve and associated equipment, as shown in Figure 1, are needed to effect the desired gas separation on a continuous basis. The feed gas is introduced into Bed I. When the bubble of oxygen departs from Bed I, it is diverted to the oxygen product line. When the transition region between the oxygen and krypton leaves Bed I, it is diverted to Bed II. After this transition zone passes and concentrated krypton begins to leave Bed I, the concentrated krypton is diverted to the

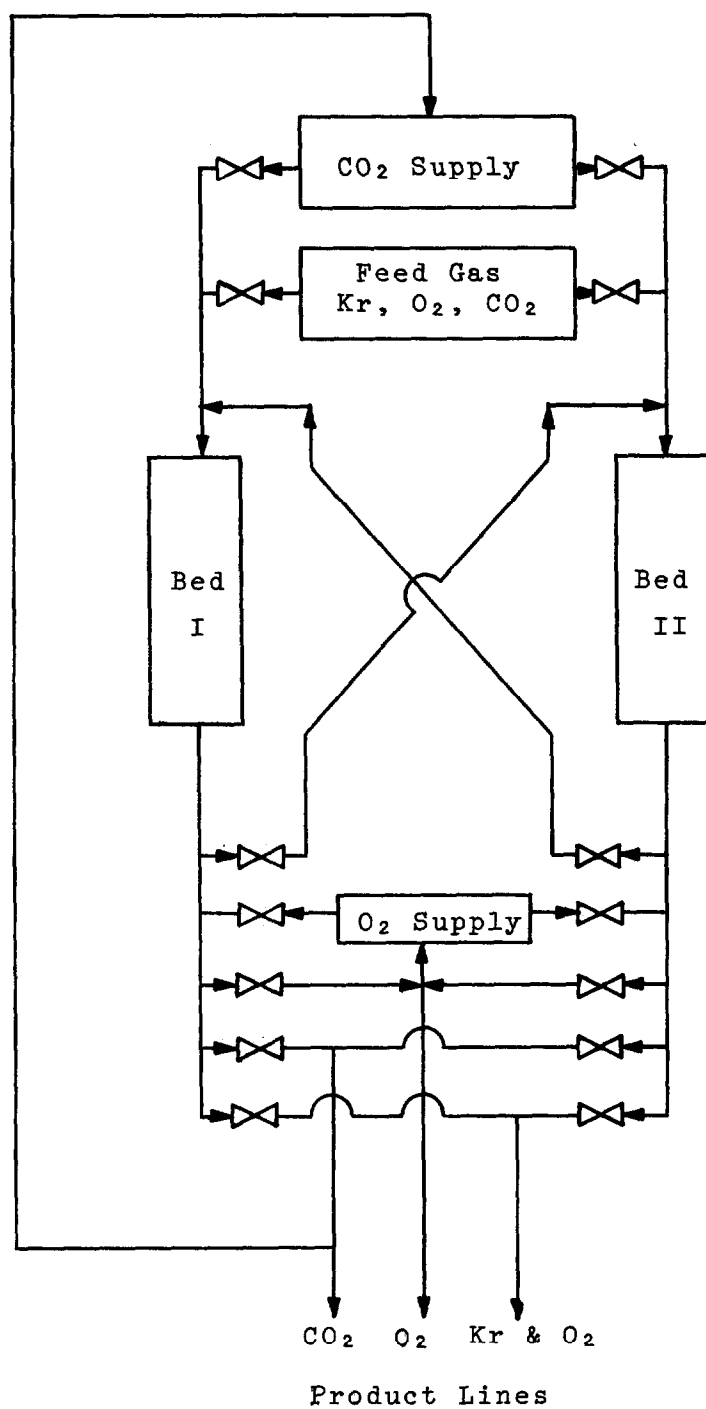


Figure 1. Process Flowsheet

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krypton product line. Finally, when the krypton-CO₂ interface exits Bed I, it is diverted to Bed II; after it reaches Bed II, the feed gas is cut from Bed I and sent to Bed II directly. At this point, Bed II undergoes the same steps that occurred in Bed I.

During the period that Bed II is adsorbing CO₂ and before the oxygen-krypton front leaves Bed II, Bed I undergoes the following steps. First, a small amount of pure CO₂ is fed to Bed I to displace the feed gas out of the void spaces and piping. This ensures that only CO₂ is present in Bed I. The small amount of gas leaving Bed I is mixed with the feed gas to Bed II. Second, Bed I is heated to at least +150°C and the pressure is decreased to near vacuum, which removes all adsorbed CO₂ from the bed. The CO₂ removed should contain little or no krypton. Third, the bed is cooled down and pressurized to system pressure with relatively nonadsorbing O₂. Bed I is now capable of handling gas from Bed II. This two-bed process, in which each bed experiences an identical cycle, can handle a constant feed gas flow and yield a highly concentrated krypton gas product. Depending upon system cycle times and economics, the process can use multiple molecular sieve beds, each bed being in a different part of the cycle. If any of the by-product O₂ or CO₂ is contaminated with radioactive krypton, it can be recycled to the front end of the primary krypton removal system, KALC.

III. Theoretical Analysis

For design purposes, it is important to be able to predict the performance and characteristics of any proposed process. Because of the extensive work on molecular sieves, the only important characteristic of this system not found in the literature is the concentration of krypton in the krypton product stream as a function of feed gas composition, bed pressure, and bed temperature. A very simple model and computer program was developed to determine this concentration. The results of these calculations are in agreement with experimental data, as discussed in the "Experimental" section.

The model can best be described by example. The following information as input data is required: temperature of the molecular sieve, gas pressure over the bed, feed gas composition, and the amount of each gas adsorbed per gram of molecular sieve as a function of temperature and the partial pressure of that gas. Adsorption data are available in the literature in the form of graphs and equations for O₂^(4,5), CO₂⁽⁶⁻⁸⁾, and Kr⁽⁹⁻¹⁴⁾. The maximum capacity for a bed of any size can be calculated from adsorption curves for CO₂.

Assume that a bed of Linde 5A molecular sieve is to be used at a constant temperature of 0°C and 1 atm of pressure. A gas with the composition of 93.09% CO₂, 1.48% Kr, and 5.43% O₂ by volume is fed to the bed. This model is based on following a unit volume through the bed. For this example, 1 cm³ of volume will be used. This volume enters the bed and is unaffected and unadsorbed until it reaches the CO₂ adsorption zone in the bed. At this time, 93.09% of the gas (the CO₂) is adsorbed onto the bed, leaving 0.0543 cm³ of O₂ and 0.0148 cm³ of krypton. Given that the CO₂ partial pressure

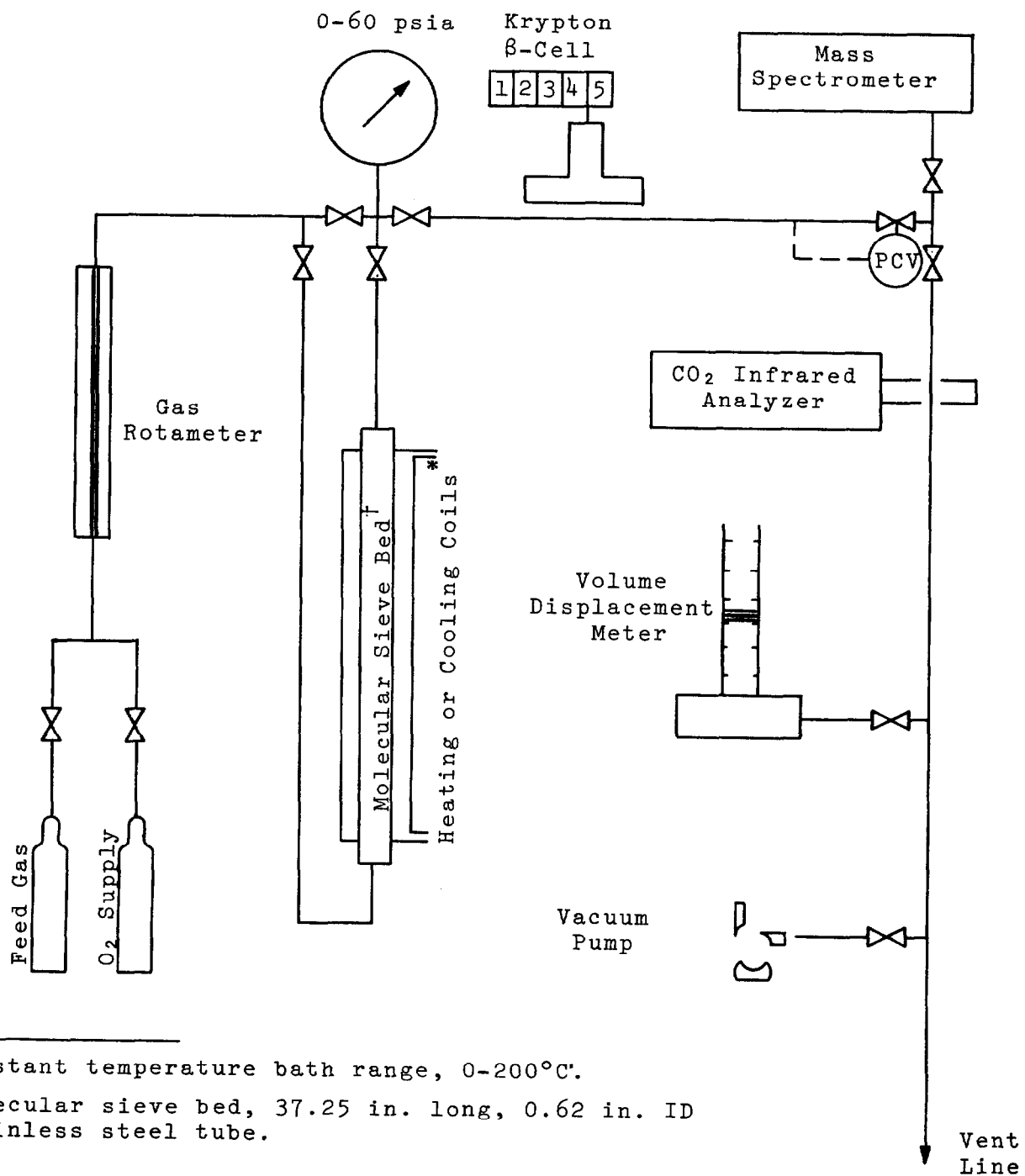


Figure 2. Simplified diagram of experimental apparatus.

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of the feed gas is 0.9309 atm, 0.9309 cm³ of CO₂ can be adsorbed on 0.010442 g* of 5A molecular sieve at 0°C. An iterative procedure is required to determine how much krypton gas was pushed off this 0.010442 g by the CO₂. For an initial estimate of the krypton gas pressure in the zone with no CO₂, the total pressure is multiplied by 0.0148/(0.0148 + 0.0543), which is the ratio of krypton in the feed gas to the krypton and oxygen in the feed gas. Given this krypton gas pressure of 162.77 torr and 0.010442 g of Linde 5A molecular sieve saturated with krypton, the amount of krypton calculated to be on the molecular sieve is 0.0363573 cm³ (9). Past the adsorption front, the first calculated composition of the gas consists of 0.0148 + 0.0363573 cm³ of krypton gas plus 0.0543 cm³ of oxygen. This implies that 48.51% of the gas is krypton, or a krypton gas pressure of 368.68 torr. With this new krypton gas pressure, one recalculates the amount of krypton adsorbed on 0.010442 g of molecular sieve and recalculates a new gas composition. This iteration is continued until convergence on a final gas composition is achieved. For this example, the composition of the final gas is 71.49% krypton and 28.51% O₂. In theory, one expects some krypton to remain on the molecular sieve in the presence of CO₂; however, experiments showed that the equilibrium adsorption is so favorable toward CO₂ that this amount of krypton can be ignored.

There is a slight adsorption of oxygen on a clean bed; thus this method must be repeated for the oxygen-krypton transition region in order to determine the exact amount of oxygen desorbed per unit of feed gas introduced. If the bed is initially saturated with oxygen and feed with a low oxygen content is used, this slight correction becomes significant.

IV. Experimental Program

Equipment

Figure 2 shows a sketch of the experimental apparatus used to test and verify that the proposed process works. This apparatus can duplicate conditions in one column of the proposed process. Most experimental runs involve feeding a gas of known composition, flow rate, pressure, and temperature into a molecular sieve bed of known composition and observing the composition, flow rate, pressure, and temperature of the exit gas as a function of time. To ensure a feed gas of known and constant composition, the gas was premixed, analyzed by several techniques, and then stored in a standard gas cylinder. For accurate analysis, the krypton was spiked with radioactive ⁸⁵Kr, which allowed the use of accurate on-line beta radiation detection cells⁽¹⁵⁾ to measure krypton concentration as a function of time. The CO₂ was analyzed by a Beckman 315A infrared analyzer. A mass spectrometer was used to verify the absence of any significant system contamination.

*This calculation assumes that commercial molecular sieve containing 20 wt % clay binder is used and that the equivalent of 0.02 g of CO₂ per gram of molecular sieve is already on the molecular sieve as a result of earlier incomplete bed desorption and/or bed degradation.

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Choice of Molecular Sieve

Type 4A and 5A molecular sieves were tested experimentally. Screening tests showed that, while 4A was capable of removing CO₂, it did not adsorb significant amounts of krypton and its adsorption kinetics for CO₂ were slow as compared with 5A. Initial tests on molecular sieve 5A showed excellent performance characteristics; hence all major work was done with 5A molecular sieve. The following parameters characterize the 5A molecular sieve that was used:

Properties of 5A Molecular Sieve

Type: 5A (commercially produced form)
Manufacturer: Union Carbide Corporation, Linde Division
Form: 1/16-in. pellets, ~3/16 in. long
Composition: Calcium form of alumina-silicate crystals, Type A
Analysis⁽¹⁶⁾: ~80% active crystalline material, ~20% inert clay binder
Density (minimum): 40 lb/ft³
Heat of Adsorption for CO₂: 12,500 cal/mole
Heat of Adsorption for Kr⁽⁹⁾: 3720 cal/mole
Heat of Adsorption for H₂O (max): 18,000 cal/mole

Experimental Variables

During all of the experimental runs, the molecular sieve was kept in a constant-temperature bath at 0°C. The composition of the feed gas was 93.09% CO₂, 5.43% O₂, and 1.48% krypton with ⁸⁵Kr tracer. The system pressure was varied from 1 to 2.5 atm, while the feed gas flow was varied from 1.494 x 10⁻² g per minute per square centimeter of molecular sieve bed cross section [7.62 cm³(STP)/cm²-min] to 29.964 x 10⁻² g/cm²-min (152.86 cm³/cm²-min). When it was desired to strip the molecular sieve of CO₂, the bed was heated to at least 150°C for 8 hr under vacuum provided by a mechanical vacuum pump and purged with oxygen several times during bakeout.

Experimental Results

Table I and Figure 3 present some of the experimental data collected. The following results were obtained:

- (1) In all runs where the bed was carefully desorbed of CO₂, the concentrations of CO₂ in the oxygen bubble and the oxygen-krypton product were below the limit of CO₂ detection (10 ppm) by the instrumentation being used.
- (2) No krypton has been detected in the oxygen bubbles expelled from the bed. This implies a krypton decontamination factor of at least 1000, i.e., that the krypton concentration in the oxygen is not more than 1/1000 the krypton concentration in the feed gas.
- (3) Mass transfer between CO₂, krypton, and the adsorbing surface is fast and does not limit the performance of a molecular sieve bed under reasonable operating conditions. Table 1 shows the length of the krypton-CO₂ mass transfer zone within the molecular sieve bed. Note that this length is only about three times that of the molecular sieve pellets (0.5 cm). The mass

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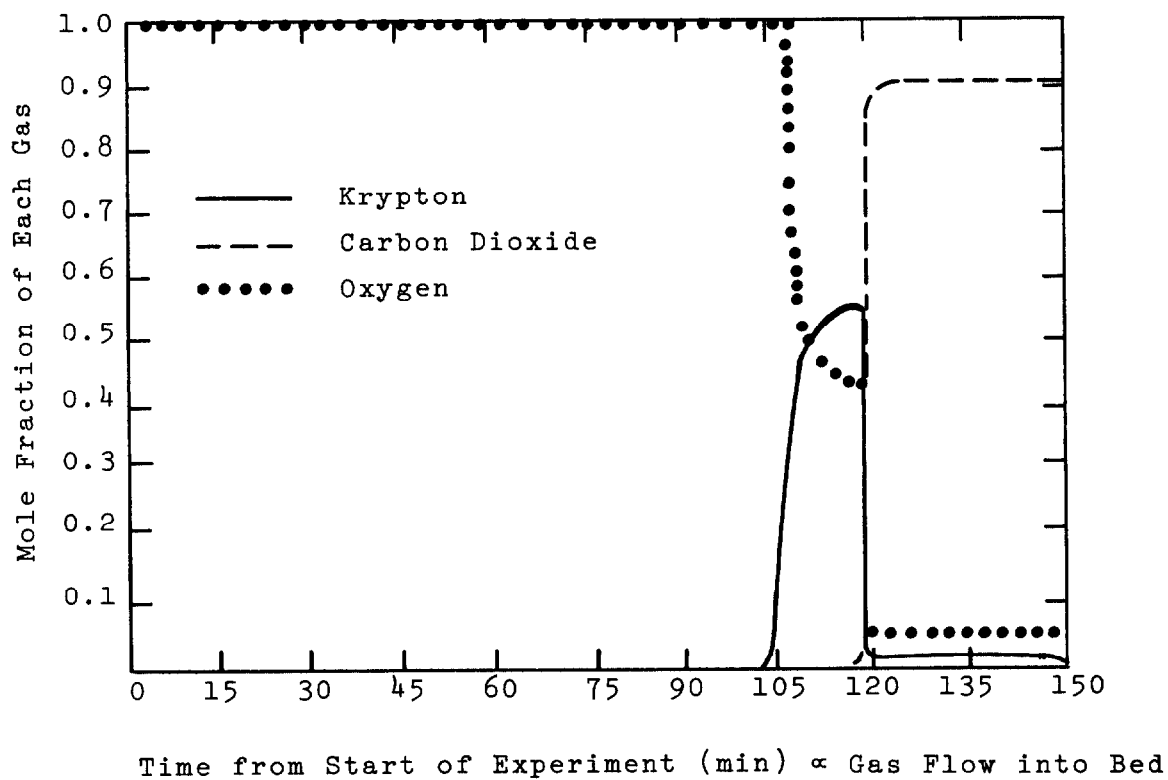
transfer length is defined as the minimum distance through the bed where the concentration of krypton changes by 90% of the difference between its peak values and its value in the feed. A mass transfer zone, at most a few centimeters long in a bed that is several meters long, does not limit bed performance or operation. Figure 3, which is a plot of the concentration of krypton exiting from the bed as a function of time for a single run, is nearly a discontinuous function between the krypton product wave and the feed gas coming through the bed. Unlike some other uses of molecular sieves, mass transfer is not a limiting factor in performance here.

- (4) Starting with a feed gas containing 1.48% krypton, the concentrations of krypton in the product streams of all experiments exceeded 50%. This implies removal of all CO₂ and significant separation of O₂ from krypton since the maximum krypton concentration possible by removal of CO₂ is 21.4%. Table 1 shows the krypton product concentration. From theory, a krypton concentration of 71.5% would be expected at 0°C and 1 atm of pressure with the above feed gas. Note that the predicted krypton concentration is higher than the experimentally determined concentration. Adsorption of CO₂ releases large amounts of heat (12,500 cal/mole) which result in a decrease in the adsorption of krypton. This decrease, according to the model, results in a decrease in the maximum krypton concentration. It is believed that a rising internal bed temperature caused this difference between theory and experiment. The column labeled "Implied Temp. Difference" in Table 1 shows how much the bed temperature must be heated above 0°C in order for the model to fit experimental results. As a point of comparison, the heat of adsorption of the CO₂ on the molecular sieve would be sufficient to increase the temperature of the bed to 240°C if there was no cooling and if higher temperatures did not desorb CO₂ and thereby reverse the heat effects. This temperature effect indicates that the limiting design condition for a molecular sieve bed in the proposed process is the rate at which heat of adsorption can be removed from the bed.
- (5) The capacity of the molecular sieve to adsorb CO₂, using the manufacturer's data⁽⁶⁾, is 94.2 cm³/g at 0°C, 1 atm of pressure, and a gas composed of 93.09% CO₂. This value agrees with the experimental results shown in Table 1. The experimental data show considerable scatter because the amounts of CO₂ entering and leaving the experimental apparatus are simply measured by rotameters over a period of several hours - a technique which is not designed to obtain accurate values. At these CO₂ partial pressures, the molecular sieve is approaching saturation and small changes in pressure have little effect on the amount of CO₂ adsorbed.
- (6) Preliminary molecular sieve bed desorption runs have been made by heating the bed to 150°C. The results indicate that the CO₂ evolved from the bed has less than 1/50 of the krypton that the feed contained. This is an upper limit. Future work after equipment modifications should be able to more accurately measure this ratio.

Table I. Experimental results

Run number	Pressure (atm)	Flow rate $\frac{\text{cm}^3}{\text{min}}$ ^a	Length of mass transfer zone (cm)	Max. krypton concentration (%)	Implied temp. difference (°C)	CO ₂ adsorbed (cm ³ /g) ^b
1	1.0	7.6	1.0	52.3	30	89.8
2	1.0	34.1	2.3	55.6	25	93.9
3	1.0	49.9	1.0	58.0	21	103.5
4	1.0	76.2	1.4	56.2	24	93.5
5	1.0	91.7	1.5	55.5	25	99.6
6	1.14	48.0	1.1	58.6	-	87.9
7	1.14	48.9	1.1	58.2	-	93.8
8	2.36	50.3	2.1	51.6	-	94.6
9	2.36	96.4	3.1	61.8	-	96.6
10	2.36	152.9	2.3	57.4	-	93.1

^aGas at standard temperature and pressure.^bGas at standard temperature and pressure adsorbed per gram of molecular sieve.



Molecular Sieve: Linde 5A
 Feed Gas: 93.09% CO₂, 5.43% O₂, 1.48% Kr
 Bed Conditions: 0°C, 1.14 atm
 Feed Gas Flow: 48.9 cm³(STP)/cm²-min
 Bed Length: 94.6 cm (37.25 in.)

Figure 3. Gas composition from molecular sieve bed vs time.

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V. Conclusions

Experiments have shown that 5A molecular sieve can separate krypton and oxygen from bulk amounts of CO₂ while partially separating the krypton from the oxygen. This process should be a reliable, economic way to separate bulk CO₂ from semiconcentrated radioactive krypton in a nuclear fuel reprocessing plant. Future experiments are planned to more accurately assess temperature transient effects in the system as well as in systems with xenon gas added.

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DISCUSSION

COLLARD: Did you investigate the behavior of ozone due to krypton 85 radiation on the adsorption column?

FORSBERG: We have not investigated ozone yet. We don't think there should be a problem but we're going to be doing some more literature searches on that area. We have, of course, although it was done after I submitted this paper, investigated effects of xenon through one of these beds. You first get an oxygen peak, a krypton peak, a xenon peak, and then the feed gases. So there's no problem in that respect.

CLOSING REMARKS OF SESSION CHAIRMAN:

In this session you've heard a lot about krypton removal and very little about Carbon 14 or tritium removal. You have heard even less about what we're going to do with any of these removed species. I believe that the momentum of these conferences is going to continue and that there will be a 15th Air Cleaning Conference in two years. As a means of summarizing this session, I would like to see the 15th Air Cleaning Conference, address two major things; first, on the part of the rulemakers and policymakers, whether we have reached an international consensus on removal of these species or not. I think we should hear much more about that subject in two years.

Second, if we are going to remove them, then we should be hearing much more about finished processes for krypton removal and much more about what we're going to do about the other two isotopes and particularly, in all three cases, what are we going to do in the way of temporary storage or permanent disposal of all three of these isotopes.

With that as an intervening charge for the next two years, a lot of people are going to have to be pretty busy in this field.